The chemistry of half-sandwich vanadium imido-amido complexes

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The chemistry of half-sandwich vanadium imido-amido complexes

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Chapter 1

Introduction: vanadium(V) cyclopentadienyl amido-imido complexes

In this introductory chapter, the combination of the cyclopentadienyl and imido ligands on vanadium(V) will be introduced. The reactivity of the metal-nitrogen bonds in hydroamination reactions is investigated and the different behavior of rare-earth transition metals vs. early transition metals towards unsaturated substrates will be discussed. The most common mechanism proposed for lanthanides in hydroamination reactions identify the metal-amide bond as the catalytically active species, whereas for the group 4 metals the active species is the metal-imido bond.

1.1 Vanadium – historical background

Right from its discovery, vanadium proved to be a challenge, being discovered 'twice', in 1801 by Andres Manuel del Rio from Mexico and in 1831 by Nils Gabriel Sefström from Sweden. Del Rio initially called the element 'panchromium' due to material properties reminiscent of those shown by chromium. Later on he changed the element's name into 'erythronium' (erythrocyte = Greek for red blood cell) just because most of the generated salts turned red upon heating. Sefström discovered the same element, naming it 'vanadium' in the honour of the Northern-Germanic tribes' goddess Vanadis (Vanadis - referring to beauty and fertility) because of its beautiful multicolored compounds. [1]

Vanadium is one of the most interesting metals among the early transition metals, exhibiting many different types of reactivity due to its ability to adopt a plethora of oxidation states (-1 to +5).[2] For this reason, vanadium compounds have been intensively studied, in particular with respect to their catalytic properties. The discovery of Ziegler-Natta catalysis provided an important incentive for the application of vanadium in the catalytic polymerization of α-olefins.[3,4] The 1980s and 1990s witnessed tremendous advances in the design and performance of early-transition metal catalysts for olefin polymerization, in particular the metallocene family of catalysts.[5,6] Thus, cyclopentadienyl ligands have become the most frequently employed ancillary ligands for early transition-metal organometallics. These monoanionic ligands can effect complete aromatic delocalization of the electrons in the π-system and are therefore chemically relatively inert. Especially the group 4 metal metallocenes form an important group of catalysts from which a large variety of derivatives can be generated. An early approach to devise new, non-metallocene catalysts that are isoelectronic to group 4 metallocene catalysts is the isolobal analogy.[7] It is used to find suitable metal-ligand combinations that are likely to be effective in catalytic olefin polymerization. An important type of ligand used for this approach is the imido ligand.

1.2 The imido ligand for high oxidation state metals

Imido ligands were found to possess similar frontier orbital energies and symmetries to those of cyclopentadienyl ligands.[5] The imido moiety can contribute electron density to the metal center through a combination of one σ and either one or two π bonds. The π interactions involve the overlap of a metal *d* orbital with a *p* orbital of the ligand. As the *p* orbital of imido ligands are lower in energy than the metal *d* orbital, due to the high electronegativity of nitrogen, productive π-bonding with the metal center requires an empty metal *d* orbital, i.e. the metal center is in a high oxidation state with a low *d* electron count.[8] The electronic contribution of the imido ligand to the metal center is most clearly seen by the valence bond description (Figure 1).[9]

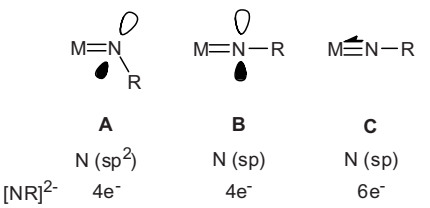
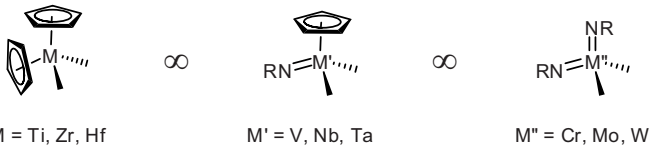


Figure 1. *Limiting valence bond descriptions of a metal-imido bond.*

Structure **A** (Figure 1) illustrates a sp^2 hybridized nitrogen leading to a M=N double bound (1σ, 1π) and a bent M−N−R linkage with the lone pair residing in a N (sp^2) orbital, which behaves as a four-electron ($4e^-$) donor. A linear M−N−R moiety **B** suggests *sp* hybridization of the nitrogen atom, this results in the lone pair residing in a pure *p* orbital. If symmetry restrictions do not allow lone-pair donation, nitrogen remains a four-electron donor and the M=N double bond (1σ, 1π) from the structure **B** is maintained. However, in most systems lone-pair $p(\pi) \rightarrow M(d)$ donation is very effective, leading to the linear structure **C** and a M≡NR bond with a bond order of 3. In the last scenario, the imido dianion $[NR]^{2-}$ is a formal six electron ($6e^-$, 1σ, 2π) donor to the metal.[7]

Combination of a cyclopentadienyl ligand and an imido ligand on a group 5 metal results in half-sandwich imido species CpM(NR), which have frontier orbitals with symmetry properties similar to those of group 4 metallocene species Cp_2M (Scheme 2).[10]



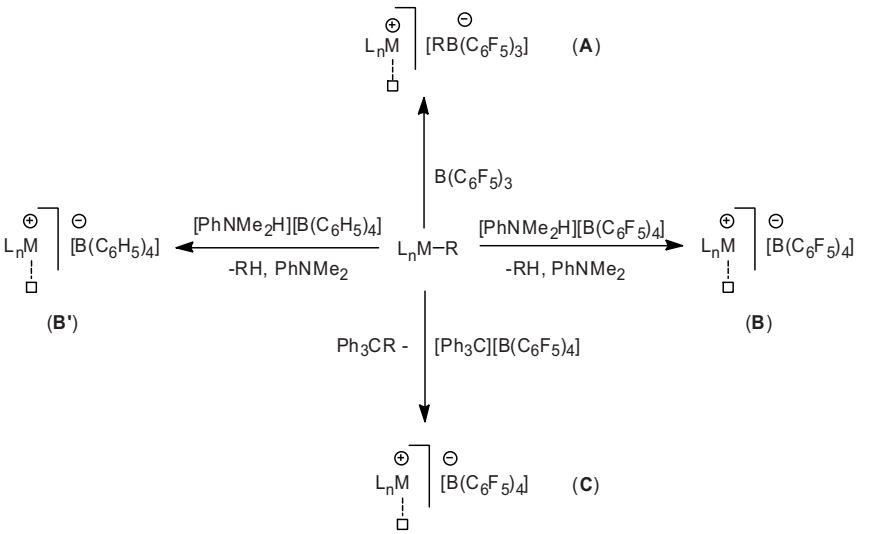
Scheme 1

The isolobal relationship model, which derives from the similarities between the symmetry properties of the frontier orbitals of the imido and cyclopentadienyl ligands, has been successfully employed to prepare catalysts based on vanadium(V),[11,12,13] niobium and tantalum,[14,15] and was also extended to non-cyclopentadienyl bis (imido) complexes of the group 6 metals (Scheme 1).[10]

1.3 Routes toward cationic complexes

In transition metal-catalyzed processes, it is generally required that the metal center has a certain degree of electronic unsaturation (at least for the capture of substrates, which in most cases have Lewis basic properties). For olefin polymerization catalysis, a valence electron count of 14 v.e. or less of the catalyst species before substrate binding is required for efficient catalysis. Cationic catalyst species tend to be the most efficient in this type of catalysis, and various methods are available to generate those from neutral metal alkyl complexes as catalyst precursors (usually with a weakly nucleophilic anion as counterion).[16] As the metal-alkyl moieties of neutral early transition metals complexes are significantly more nucleophilic than those in late transition-metal complexes, they are highly reactive towards Brønsted/Lewis acids (*e.g.* $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][BAr_4]$ (Ar = C_6H_5, C_6F_5), or $B(C_6F_5)_3$) (Scheme 2). Whereas the trityl reagent is an alkyl abstracting agent, producing an alkyl-substituted triphenylmethane, the anilinium salt removes the alkyl ligand by protonation, liberating an alkane and generating the Lewis base *N*,*N*-dimethylaniline as co-product (Scheme 2, **B** and **C**, respectively).[17,18,19] The protonation of L_nMR with the Bronsted acid $[PhNHMe_2][BAr_4]$ (Ar = C_6H_5, C_6F_5) generates a cationic metal center with the weakly coordinating anion $[BAr_4]^-$ (Scheme 2, **B** and **B'**), but possible coordination of the $PhNMe_2$ might hamper the catalytic activity of the unsaturated metal center. Reaction of a neutral methyl

precursor with the neutral Lewis acid $B(C_6F_5)_3$ results in abstraction of the methyl group and formation of alkyl borate anion (Scheme 2, **A**).[20,21,22] The latter will always be in proximity of the cationic center and residual coordinative contacts between the cationic metal center and the anion via the abstracted methyl group have been identified,[21a,23,24] but appear to be weak enough in most cases to allow the metal center to be active.



Scheme 2

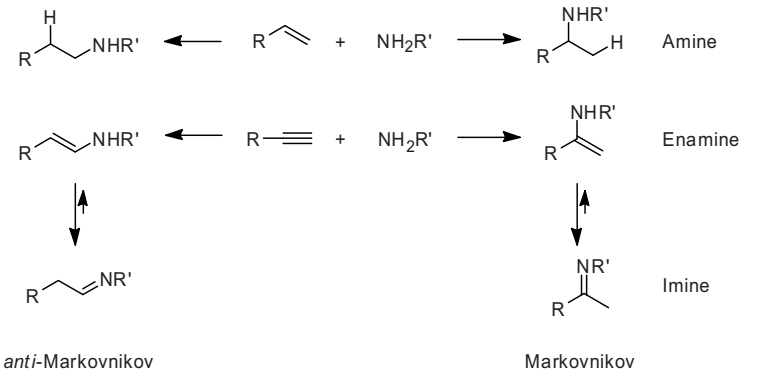
Another possible route to cationic species is by halogen abstraction from metal halide precursor with silver and thallium salts.[25]

1.4 Hydroamination, the reactivity of metal-imido and metal-amido complexes

The chemistry of nitrogen single and double bonds to transition metals has been relatively little investigated compared to that of the corresponding metal-carbon[26] bonds. The imido ligand has been employed as an ancillary group to support high-oxidation state metal centers, and an increasing number of complexes having reactive imido ligands have been shown to participate in C-H bond activation,[27] cycloaddition[28] and metathesis reactions[29]. In particular, group 4 imido[9,30] complexes play a pivotal role in various important catalytic processes, such as, the intermolecular hydroamination of alkynes,[27e,31] alkenes,[32] hydrohydrazination of alkynes,[33] three-component coupling reactions to form α,β-unsaturated β-aminoimines,[34] guanylation of amines[35] and carboamination processes.[36]

The catalytic addition of an N-H bond across unactivated C-C multiple bonds[37] is one of the most direct and efficient methods of alkylating an amine. Over the past decade there has been a growing effort to develop efficient and selective catalysts for this apparently simple but challenging transformation. The major problem of amine additions to non-activated alkenes and alkynes is the electrostatic repulsion between the lone pair electrons of the nitrogen atom and the electron rich π-system of the unsaturated compound. This repulsive interaction results in high activation barriers for the corresponding uncatalyzed reactions.[38] As a result, catalysis seems to offer the only possibility to realize the desired hydroamination reactions.

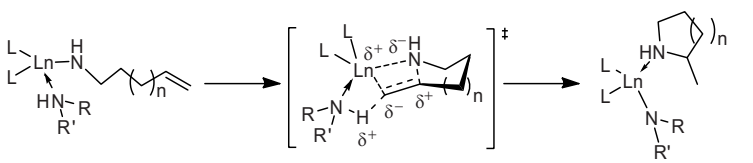
In general, direct addition of amines to unsaturated C-C bonds can lead to two regioisomeric products, the Markovnikov and the *anti*-Markovnikov products (Scheme 3). This process can be catalyzed by a range of metal complexes from across the periodic table. As is often the case, suitable catalyst-substrate combinations need to be found in order to obtain the desired activity and selectivity for the transformation.



Scheme 3

1.4.1 Rare-earth metals in hydroamination processes

Rare-earth metal complexes are highly efficient catalysts for *intra*molecular hydroamination of various C-C unsaturated compounds such as (terminal) aminoalkenes,[39] aminoalkynes,[40] aminoallenes,[41] and aminodienes,[42] whereas *inter*molecular hydroamination reactions are significantly more challenging and only a limited number of successful catalysts (either lanthanocene[43a,b] or lanthanide binaphtholate[43c]) have been reported in the literature. The general hydroamination/cyclization[44,45] mechanism is believed to proceed through (often rate-determining) insertion of the C-C multiple bond into the Ln-N bond, followed by rapid protonolysis of the resulting Ln-C bond by additional amine substrate (Scheme 4).



Scheme 4

The lanthanide based catalysts are exceptionally well studied for *intra*molecular olefin hydroamination.[46,47] It was shown that catalytic activity of lanthanide based catalysts in hydroamination/cyclization of aminoalkenes increases with increasing ionic radius of the rare-earth metal and a more open coordination sphere around the

metal (Figure 2),[48] whereas the hydroamination/cyclization of aminoalkynes follow the opposite trend.[40] Generally, the rate of cyclization can be summarized as follows: aminoalkyne > aminoallene > aminoalkene.

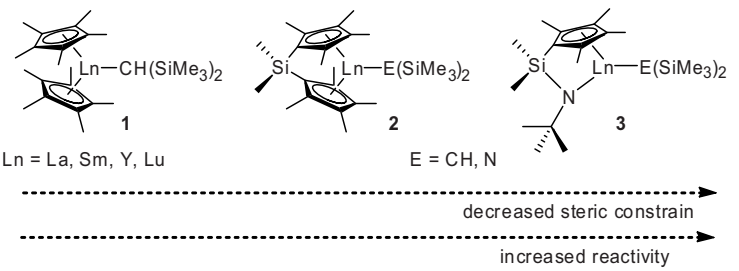


Figure 2. *Influence of steric constraints on catalyst reactivity.*

Although most of the early rare-earth metal catalysts for hydroamination/cyclization bear cyclopentadienyl-type ligands,[49] the development (since 1998) of cyclopentadienyl-free rare-earth metal based hydroamination catalysts expanded the spectrum of available catalysts for these transformations (Figure 3).[50,51,52,53,54]

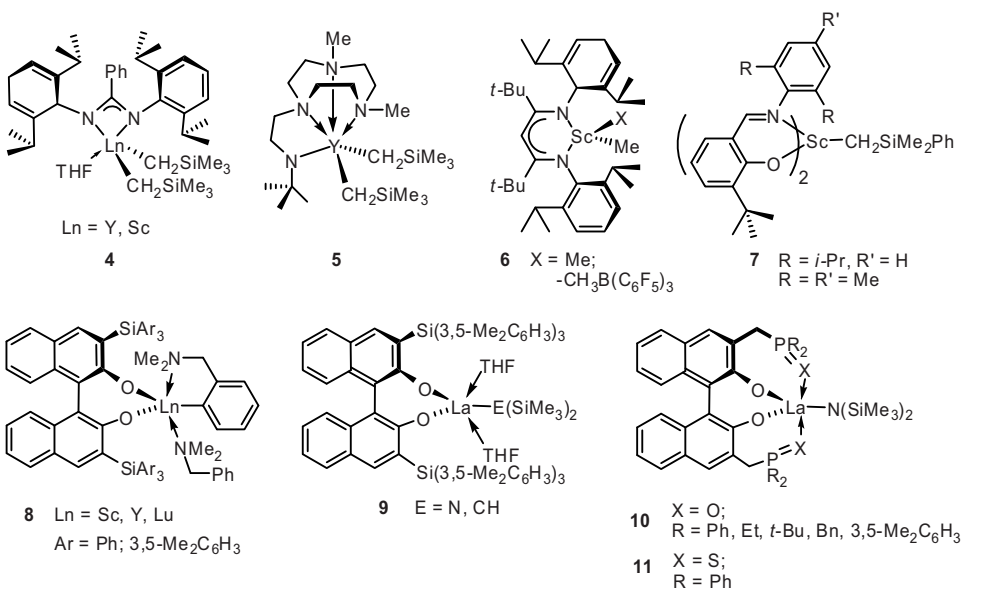


Figure 3. *Several non-metallocene rare-earth metal based hydroamination catalysts.*

The catalytic activity for hydroamination reactions usually decreases with decreasing ionic radius of the metal center. This can be overcome by a controlled substrate access to a metal center of high Lewis acidity (*e.g.* complex **6**, X = Me; complex **7**, R = *i*-Pr, R' = H). Changing the ligands around the metal the catalytic activity can be enhanced as well as the affinity towards different substrates; *e.g.* binaphtholate complexes **8** – **11** show high activity for asymmetric hydroamination/cyclization reactions.[55]

While *intra*molecular hydroamination reactions are efficiently catalyzed by rare-earth metal catalysts, *inter*molecular hydroamination proved to be more challenging. In this process the Markovnikov addition of *n*-propylamine to 1-pentene catalyzed by $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$ remains the state of the art.[56] However, the rare-earth metal catalyzed hydroamination of more activated olefinic substrates, for example vinyl arenes, have proven more promising and provided facile access to tetrahydroisoquinolines via consecutive hydroamination of divinylarenes.[56b]

1.4.2 Late-transition metals

A variety of late-transition metals[57] complexes have been proven active catalysts for both *intra*- and *inter*molecular hydroamination reactions and different mechanistic models that account for the observed regioselectivity have been suggested: (*i*) nucleophilic attack of the amine on a coordinated alkene or alkyne; (*ii*) nucleophilic attack of the amine on allylic complexes was proposed for hydroamination of allene,[58] dienes,[59] and trienes[60]; (*iii*) insertion of the alkene into a metal-hydride bond when the hydroamination takes place in the presence of an acid[61] and (*iv*) oxidative addition of the amine N-H bond, followed by insertion of the alkene/alkyne into the metal-amide bond and C-H reductive elimination. Whereas categories *i*, *ii*, and *iii* involve activation of the C-C multiple bond, pathway *iv* entails activation of the amine.[54]

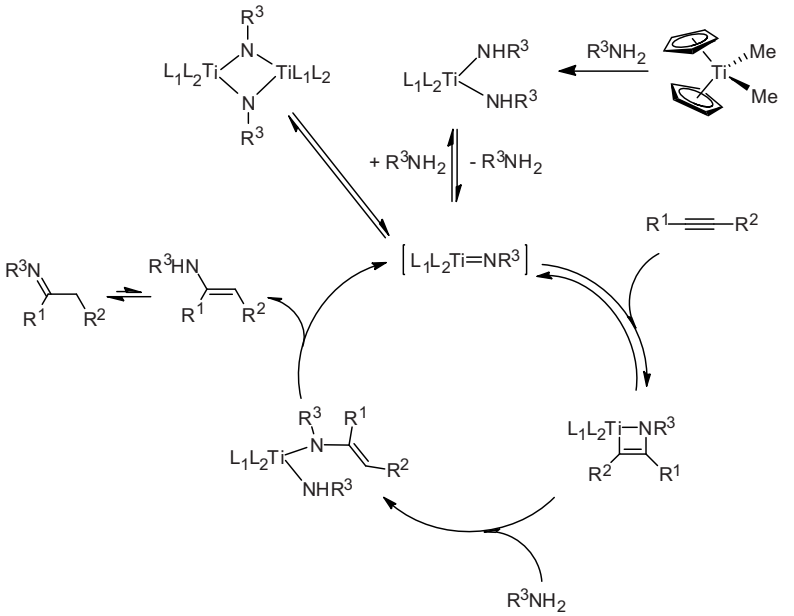
Late transition metals do not display the hard Lewis acidity and oxophilicity of the rare-earth metals and early transition metals, which results in a better compatibility with oxygen-containing substrates that would inhibit or deactivate catalyst based on highly oxophilic metals. Catalytic systems using ruthenium,[62,63,64] rhodium,[65] and palladium-complexes[66] have been described. Cd^{II} and Hg^{II} were investigated in

early studies also, but their toxicity makes them less desirable for practical application.[54] Palladium is the most employed metal in the catalytic hydroamination of alkynes.[67] The most research was aimed at *intra*molecular hydroamination and only a few examples concerning *inter*molecular hydroamination were reported.[54,68] Concerning *intra*molecular hydroamination, η^2-alkyne-organo-palladium complexes were extensively used for the synthesis of heterocyclic compounds, in particular in the synthesis of indoles.[69] The versatility of the palladium-catalyzed intramolecular hydroamination of alkynes has been demonstrated in the construction of other structurally very interesting heterocycles such as lactams, oxazolidinones, dupyrrins, pyrroles, and pyrazoles. [70]

Although late transition metals display high functional group compatibility, the main drawbacks of the use of these metals are their relatively low activity and scope outside *intra*molecular hydroamination.[54]

1.4.3 Early transition metals

Early transition metals are widely investigated as catalysts for *inter*- and *intra*molecular hydroamination reactions, as they shown significant advantages compared to those based on toxic (Hg, Tl) or more expensive metals (Ru, Rh, Pd, etc.). In contrast to rare-earth metals, where the active species involves a metal-amido bond, for the group 4 metals, the catalytically active species is believed to be a metal-imido complex. However, when a metal-imido-amido catalyst species is present, the involvement of the metal-amido bond in the main catalytic pathway cannot be excluded (experimentally and theoretical studies).[71,72] The mechanism of group 4 metal catalyzed hydroamination of alkynes and allenes has been thoroughly investigated in detailed kinetic, mechanistic,[73] and computational studies.[74] On the basis of these studies, the dominant pathway is the following: a metal-imido species undergoes a reversible [2 + 2]-cycloaddition with an alkyne (or allene) to yield an azametallacyclobutene species (Scheme 5),[73,75] followed by protonation of the M-C bond of the metallacycle by the amine.



Scheme 5

The product is released and the metal imido species is regenerated via reversible α-elimination of an amine from a bis(amido) precursor. Depending on the steric demand of the imido ligand and the ancillary ligands, the imido species can be in equilibrium with the imido-bridged dimer, favoring the dimeric species with minimalized steric interactions between the ancillary and imido ligands.

A large number of titanium-based hydroamination catalyst systems have been developed (Figure 4) and have been subject of several reviews.[31f-g,37a,54] Titanium based catalysts can roughly be divided into 2 groups: those with cyclopentadienyl ligands and those without. Some of them are readily available and relatively cheap while others can be generated in situ. Titanium complexes are particularly useful as catalysts for the *inter*- and *intra*molecular hydroamination of alkynes and allenes. *Inter*molecular hydroamination of internal alkynes (symmetric alkynes) with sterically demanding primary amines (*e.g.* anilines, *tert*-butyl amine) catalysed by the readily available Cp_2TiMe_2 (**12**) complex was extensively studied by the group of Doye,[76] and Bergman[77]. This catalyst provided hydroamination products in good yields, whereas with less sterically congested amines such as benzyl or *n*-hexyl amines were found to react more slowly. Unsymmetrical alkynes such as 1-

phenylpropyne reacted with aniline exclusively to the *anti*-Markovnikov isomer. Better results for less sterically demanding amines are obtained with the sterically more encumbered catalyst $Cp^*_2TiMe_2$ (**13**) although hydroamination of unsymmetric alkynes gave predominantly a mixture of regioisomers. Only when *p*-toluidine was used *anti*-Markovnikov products were obtained with high regioselectivity.[78] One of the most general catalysts fo the hydroamination of internal and terminal alkynes is Ind_2TiMe_2 catalyst (**14**).[79] Unsymmetrical 1-phenyl-2-alkylalkynes and terminal alkynes were hydroaminated with modest to excellent anti-Markovnikov regioselectivity while terminal alkylalkynes and aniline preferentially form Markovnikov addition products.

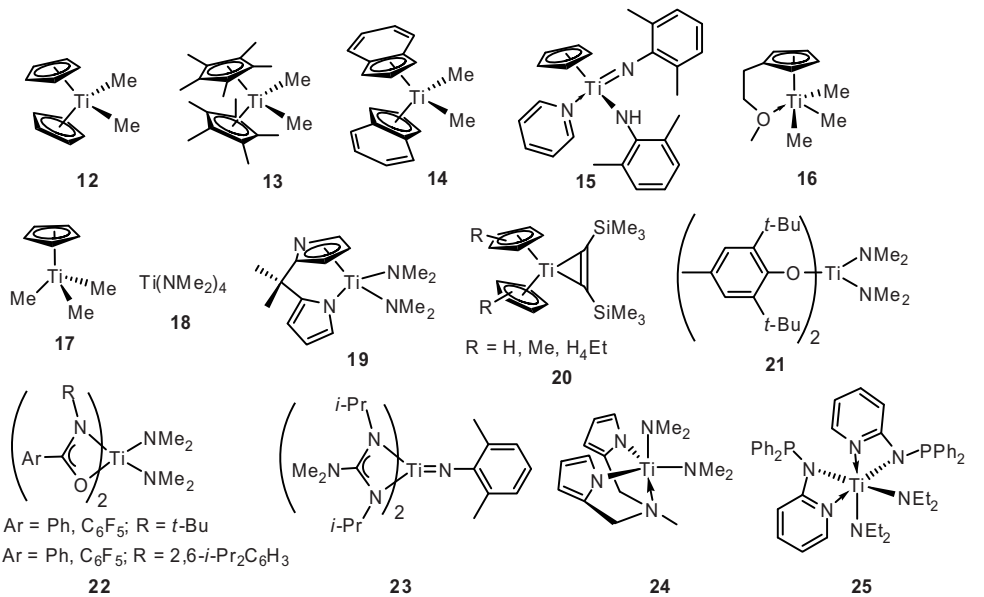


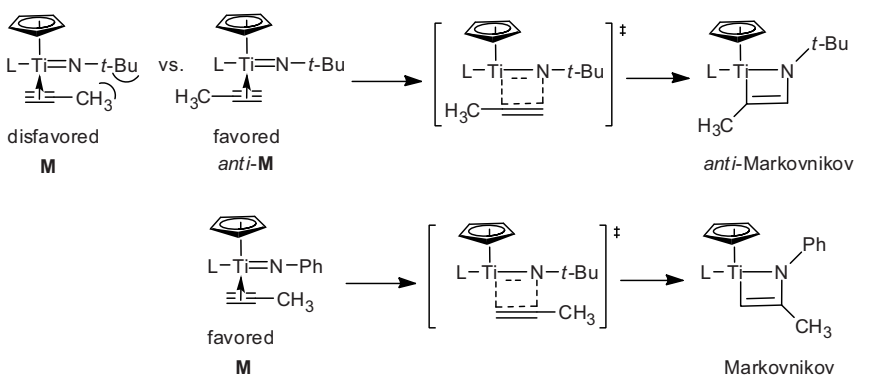
Figure 4. *Titanium-based hydroamination catalysts.*

Using Cp_2TiMe_2 as precursor for the hydroamination reactions, Doye suggests the formation of an active titanium imido species by loss of methane. However, this species was never observed directly under catalytic conditions in the reaction mixture. A in depth investigation of this system revealed the formation of a half-sandwich titanium imido amido complex, which could be isolated as its pyridine adduct Cp(ArNH)Ti(NAr)(py) (**15**) starting from Cp_2TiMe_2 and 2,6-

dimethylaniline.[77] Complex **15** is a highly effective hydroamination catalyst for alkynes and allene substrates.

The commercially available $Ti(NMe_2)_4$ complex (**18**) proved to be a viable hydroamination catalyst for internal and terminal alkynes with aryl- and alkylamines, giving moderate to excellent Markovnikov selectivity.[80a-c] Better Markovnikov selectivities for hydroamination of terminal alkynes were found in the presence of the di(pyrrolyl) amine complex **24** (Figure 4).[80d] Group 4 metal based catalysts, such as $Ti(NMe_2)_4$, $Zr(NMe_2)_4$ and the bis(aminopyridinato) complex **25** (Figure 4) proved to be good catalysts for the intermolecular ring-opening hydroamination of methylenecyclopropanes also.[81] Addition of the sterically demanding *t*-$BuNH_2$ to terminal aliphatic alkynes gave the anti-Markovnikov product with high (> 98%) regioselectivity in the presence of η^2-alkyne titanocene $Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (**16**, R = H).[31e] Sterically less demanding aliphatic amines produced anti-Markovnikov adducts also, albeit with reduced regioselectivity. The use of aromatic amines predominantly led to the Markovnikov product in which the regioselectivity correlated with the steric demand of the aniline derivative.

A computational study revealed that the regioselectivity is determined by the relative stability of the imido alkyne complex that preceeds the [2 + 2] cycloaddition step (Scheme 6).[31e] The preference for anti-Markovnikov addition for *t*-$BuNH_2$ can be based on a repulsive steric interaction of the *tert*-butyl substituent with the aliphatic substituent of the alkyne in the imido alkyne intermediate **M** leading to the Markovnikov product.

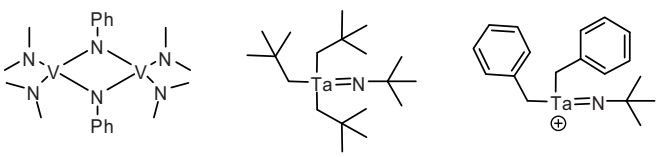


Scheme 6

The Markovnikov regioselectivity for aromatic amines on the other hand is based on the favorable alternating positive and negative charges in the Markovnikov imido alkyne intermediate **M′**.

Although early transition metals proved to be very efficient catalysts in hydroamination reactions of alkynes, it took until 2004 to find catalysts (consisting either of neutral or cationic group 4 metal complexes) that were able to catalyze *intra*molecular hydroamination/cyclization reactions of alkenes.[82] For these transformations, two distinct mechanisms were proposed for the group 4 metal-catalyzed hydroamination of aminoalkenes, mainly divided along the substrate type (primary or secondary amine), although this distinction does not hold up for all neutral group 4 metal catalyst systems.[54] For conversion of secondary aminoalkenes, by a catalytically active cationic zirconium amido species, the mechanism is believed to be similar to that proposed for rare-earth metals, whereas for primary aminoalkenes, neutral species with a metal-imido bond are denoted as the active species.

Several group 5 metal based catalyst systems, such as the imido-bridged dimer $[V(\mu^2\text{-NPh})(NMe_2)_2]_2$ (**26**),[83] the tantalum alkyl imido complex $[(Me_3CCH_2)_3Ta{=}NCMe_3]$ (**27**),[84] or the more electronically unsaturated cationic complex $[(PhCH_2)_2Ta{=}NCMe_3]^+[B(C_6F_5)_4]^-$ (**28**),[84] have been shown to be viable precatalysts for the hydroamination of terminal and internal alkynes, as well as allenes, though their catalytic activity is inferior to group 4 metal catalysts.



26 **27** **28**

Figure 5. *Group 5 based metals hydroamination catalysts.*

The proposed mechanism for group 5 metals is believed to be analogous to that of neutral group 4 metal catalysts, involving a [2+2] cycloaddition of the unsaturated hydrocarbon with a metal-imido bond, followed by protonation of the resulting metallacycle with a primary amine, regenerating the metal imido catalyst.[83,84a]

1.5 Aim and outline of this thesis

In the previous sections it was shown that early transition metal complexes can be effective catalysts for hydroamination reactions. It is generally assumed that for these metals the active species requires the presence of a metal-imido bond, although for complexes that contain both a metal-amido and a metal-imido moiety, insertion of the C-C unsaturated bond into the metal-amido bond can not be excluded. Moreover, it was shown that in the cationic cyclopentadienyl-amido complex $[(\eta^5\text{-}C_5H_4C_2H_4N\text{-}i\text{-}Pr)V(N\text{-}t\text{-}Bu)(BrC_6H_5)][MeB(C_6F_5)_3]$, the vanadium-imido bond appears to be inert towards unsaturated substrates and that acetylenes insert into the vanadium-nitrogen single bond. The aim of this thesis therefore is to provide further insight in the relative reactivity of the metal-amido and metal-imido bonds in the half sandwich vanadium (V) complexes, with particular attention to their catalytic ability for hydroamination reactions.

The synthesis and characterization of a series of neutral and cationic half-sandwich vanadium(V) amido-imido complexes is presented in *Chapter 2*. For the generation of the electron deficient (cationic) vanadium(V) species from neutral vanadium methyl complexes, various alkyl abstraction agents (activators) were used and it was observed that these Lewis acidic species may be stabilized by the coordination of various Lewis-bases. In *Chapter 3* the thermal stability of the neutral half-sandwich vanadium(V) amido-imido compounds is investigated. Thermolysis of CpV(V) imido amido methyl complexes can generate CpV(III)-imido species, thus providing a new route to these fragments, without the use of external reducing agents. These low-valent species can be trapped, *e.g.* by phosphines, and isolated, as shown by X-Ray crystal structure determinations of several derivatives.

Chapter 4 addresses the reactivity of several vanadium(V) amido-imido complexes in the hydroamination reactions of terminal and internal alkynes with *p*-toluidine or *tert*-butylamine. The results presented show that the catalytic activity of the cationic vanadium systems is low in comparison to the isoelectronic neutral titanium compounds. Using aromatic amines (*e.g. p*-toluidine), mixtures of Markovnikov hydroamination product and a substituted quinoline product were obtained. The substituted quinoline derives from a secondary reaction of the anti-Markovnikov product, which is consumed in the process. With the sterically

demanding *t*-$BuNH_2$, addition to terminal alkynes proceeds to give the anti-Markovnikov product.

In *Chapter 5*, the synthesis and characterization of neutral and cationic cyclopentadienyl vanadium (V) imido-amido complexes with a pendant arene group on the cyclopentadienyl ligand is presented. In addition, the chapter describes the thermal decomposition of the neutral *ansa*-Cp-arene vanadium (V) species. This chapter presents also a study of the cationic species and X-ray crystallographic studies provide structural evidence for intramolecular η^1-arene bonding of the pendant arene group to the cationic vanadium center. The strength of the interaction between the pendant arene moiety and the cationic metal center in complexes of vanadium(V) decreases by changing the length of the bridge between the Cp and arene moieties from a C_1-bridge to a C_2-bridge.

1.6 References

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Chapter 2

Synthesis and characterization of neutral and cationic vanadium(V) amido and imido complexes

The synthesis of neutral cyclopentadienyl vanadium(V) amido-imido alkyl complexes is discussed, followed by generation of derived cationic species. These are formed by reaction with Brønsted acid ($[PhNMe_2H]^+$) or Lewis acids ($[Ph_3C]^+$ or $B(C_6F_5)_3$). The presence of a Lewis base such as THF–d_8 or $PhNMe_2$ stabilizes vanadium amido-imido cationic species by coordination to the metal center, although this may diminish subsequent catalytic activity. Cationic species solvated by the weak nucleophile bromobenezene(-d_5) were obtained by applying the Lewis acid reagents in this solvent. In bromobenezene(-d_5) solution the cationic species with the $[MeB(C_6F_5)_3]^-$ counterion were observed as mixtures of solvent separated and contact ion pairs (in approximately 95:5, ratio).

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2.1 Introduction

Monocyclopentadienyl (half sandwich) complexes of the transition metals are versatile compounds that are used in a broad range of catalytic processes *e.g.* polymerization,[1,2,3,4,5,6,7,8] hydroamination,[9,10,11,12,13,14,15,16,17] and metathesis reactions. 'Half sandwich' complexes of a wide range of metals have been synthesized. The interest in such compounds of the group 4 metals[2,5,18,19,20,21,22] in particular is related to the activity of bis-cyclopentadienyl (bent metallocene/sandwich) complexes of these metals in catalytic olefin polymerization.[23] The replacement of one of the cyclopentadienyl ligands in these compounds with other (monodentate) monoanionic ligands generated a new family of catalysts, especially useful for ethylene/1-alkene 1-alkene copolymerization.[24,25,26,27] These allow the electronic and steric properties of the transition metal complexes to be tuned easily by the choice of monoanionic ligand.

In 2001, Bergman *et al.*[17] reported the synthesis of the cyclopentadienyl titanium imido amido complex Cp(RNH)Ti(NR) (**A,** Figure 1)**,** which was shown to be an efficient catalyst for hydroamination reactions (especially of alkyne substrates).

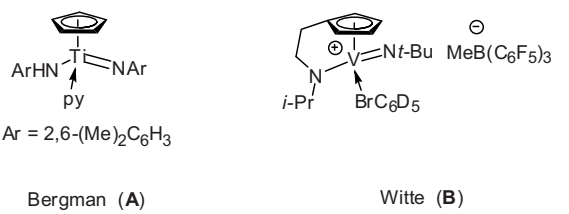
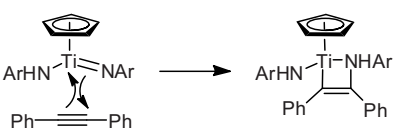


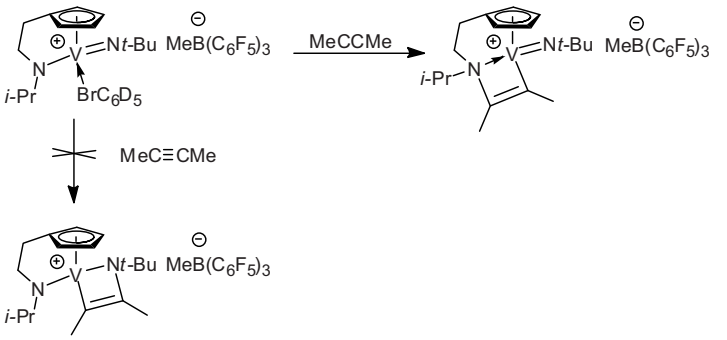
Figure 1. *Titanium and vanadium half-sandwich imido amido complexes*.

Bergman *et al*.[17] proposed (based on quantum chemical calculations and a kinetic study) that the hydroamination process involves as a reaction step the well established [2+2] cycloaddition reaction of an alkyne with the titanium imido bond (Scheme 1).



Scheme 1

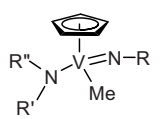
In an intriguing contrast to this, Witte *et al.*[28,29] reported that in the reaction of the isoelectronic cationic vanadium complex **B** (Figure 1) with alkynes, the acetylene inserts into the vanadium-nitrogen single bond (Scheme 2), leaving the metal-imido bond intact.



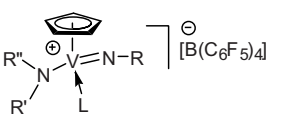
Scheme 2

Based on these results, an alternative cycle for the hydroamination reaction reported by Bergman could be drawn with an alkyne insertion into the M-amido bond rather than the [2+2] cycloaddition with the M-imido bond as the C-N bond-forming step. This result prompted us to perform an in-depth study of the relative reactivity of V-N and V=N bonds in half-sandwich complexes of vanadium.

In this chapter, the preparation and characterization of monocyclopentadienyl vanadium amido-imido methyl complexes **2.1**, **2.2** and **2.3** (Figure 2) is described. These vanadium-methyl complexes are then used as precursors for the synthesis of cationic vanadium imido-amido complexes **2.4**, **2.5** and **2.6** (Figure 2), which are isoelectronic to the neutral Ti-compound reported by Bergman *et al.*[17]



R = *t*-Bu; R"= *t*-Bu, R'= H (**2.1**)
R', R"= *i*-Pr; (**2.2**)
p-tolyl; R', R"= *i*-Pr; (**2.3**)



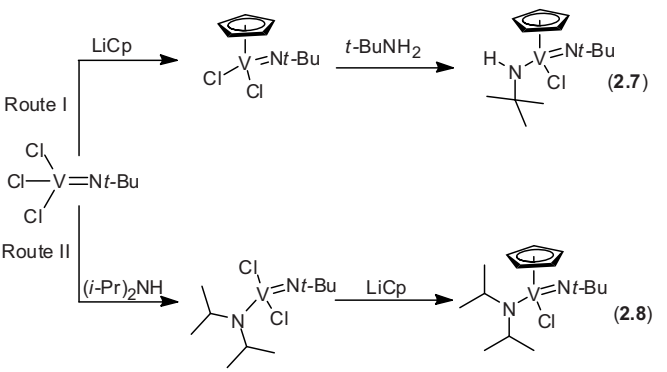
L= C_6D_5Br, R = *t*-Bu; R', R"= *i*-Pr; (**2.4**)
L= THF, R = *p*-tolyl; R', R"= *i*-Pr; (**2.5**)
L= C_6D_5Br, R = *p*-tolyl; R', R"= *i*-Pr; (**2.6**)

Figure 2. *Neutral and cationic cyclopentadienyl vanadium amido-imido complexes.*

2.2 Synthesis of neutral vanadium(V) amido-imido complexes

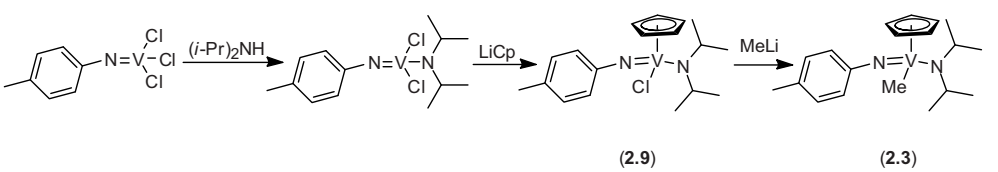
Imido vanadium trichloride complexes provide a practical entry into d^0 vanadium imido chemistry. Methods reported in the literature for the preparation of these imido precursors usually involve reaction of oxovanadium trichloride with isocyanates or amines.[30,31,32,33d]

Preuss *et al.*[33e,g] reported two routes for the synthesis of cyclopentadienyl imido-amido vanadium(V) chloride complexes (**2.7**) and (**2.8**) (Scheme 3). The first route starts with the conversion of *t*-BuNVCl$_3$ into the half-sandwich compound CpV(N-*t*-Bu)Cl$_2$ by reaction with LiCp. This is treated subsequently with two or three equivalents of a primary amine to provide Cp(*t*-BuNH)V(N-*t*-Bu)Cl (**2.7**) (Route I – Scheme 3). In the second route, the vanadium amido group is introduced in the first step to give (*i*-Pr$_2$N)V(N-*t*-Bu)Cl$_2$, which is then transformed into the desired half-sandwich vanadium complex **2.8** by reaction with LiCp (Route II – Scheme 3).



Scheme 3

In general, these procedures work well with aliphatic amido and imido groups. Witte *et al.*[28] extended this chemistry by introducing an aromatic substituent on the imido functionality, as in (η^5-C$_5$H$_5$)(*i*-Pr$_2$N)V(N-*p*-tolyl)Me (**2.3**) (Scheme 4).



Scheme 4

In order to allow a reasonable comparison in reactivity of the metal nitrogen single (amido) and double (imido) bond, it would be desirable to have the same substituent on the imido and amido groups in the complexes. In particular, *p*-toluidine and *t*-$BuNH_2$ were used since the ^1H NMR spectra of the resulting complexes are relatively simple, facilitating interpretation in reactivity studies. Unfortunately, all attempts to synthesize half-sandwich (*p*-tolylamido)-(*p*-tolylimido) vanadium(V) complexes following routes described by Preuss failed, resulting in intractable mixtures of complexes. However, half-sandwich vanadium complexes with aromatic substituents on the imido (M=N) bond are accessible *via* route II (Scheme 3). In this case, route I leads, possibly, to reduction of the metal center.[34]

The following cyclopentadienyl vanadium amido-imido chloride complexes were synthesized according to literature procedures: Cp(*t*-BuNH)V(N-*t*-Bu)Cl (**2.7**)[33e], Cp(*i*-Pr_2N)V(N-*t*-Bu)Cl (**2.8**)[33g], Cp(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**2.9**)[29]. Substitution of the chloride in **2.8** and **2.9** by a methyl group through reaction with MeLi afforded the thermally relatively labile (see below) vanadium-methyl complexes Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**), Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) in reasonable isolated yields (65-80%).

Methyl complex **2.3** is a green yellowish solid and recrystallization from pentane gave suitable crystals for X-ray structure analysis. The molecular structure of **2.3** is shown in Figure 3 and selected bond distances and angles are given in Table 1. Single crystal X-ray analysis revealed a three-legged piano stool type geometry that is typical for half-sandwich amido imido compounds of vanadium(V).[33a,g] The most notable feature of this crystal structure is the metal-imido bond. Although the slight bending in the V-N1-C6 angle of 166.2(2)º is typical for vanadium imido species (reported range V-N-C = 161 – 175º),[33g,35] the V-N(imido) bond length is slightly longer than most of the other known vanadium(V) imido complexes (V-N = 1.666(2) for **2.3**, reported V-N = 1.59 – 1.64 Å[33g,36]). An exception is Witte's system (η^5-$C_5H_4C_2H_4N$*i*-Pr)V(N-*t*-Bu)Me (**2.10**) (V-N = 1.656(2) Å).[37] The V-C_g bond length (2.006(2) Å, C_g- the centroid of the C(1) – C(5) ring) and V-N(amido) bond length (1.851(2) Å) are normal for vanadium(V).[33,35] The V(V)-Me distance (2.122(5) Å) is close to that in Witte's constrained geometry complex **2.10**

(2.103(3) Å), but slightly longer than in Nomura's (2,6-$Me_2C_6H_3N$)(*t*-$Bu_2CN)_2VMe$ (2.064 Å)[38] and in the Li[(*t*-$Bu_3SiN)_2VMe_2$] (2.043, 2.050 Å) complex.[39]

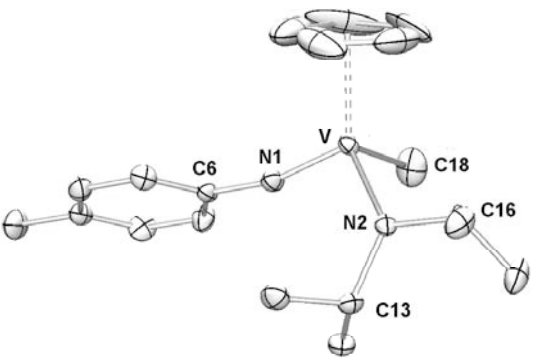


Figure 3. *Molecular structure of Cp(i-Pr_2N)V(N-p-tolyl)Me (**2.3**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.*

In its ^{1}H NMR spectrum, **2.3** shows a distinct, broad signal (δ 0.40 ppm in C_6D_6, and δ 0.62 ppm in C_6D_5Br) for the V-Me group. The broadening in the ^{1}H NMR absorptions is due to unresolved coupling with the quadrupolar ^{51}V-nucleus (*I*= 7/2). As a result of this broadening, the V-Me group in the ^{13}C NMR spectrum could not be observed.

Table 1. *Selected bond lengths (Å) and angles (°) for **2.3**.*

Bond lengths	(Å)	Bond angles	(°)
V – N1	1.666(2)	V – N1 – C6	166.2(2)
V – N2	1.851(2)	V – N2 – C13	120.5(2)
V – Cg*	2.006(2)	V – N2 – C16	126.7(4)
V – C18	2.122(5)	C13 – N2 – C16	112.7(2)
N1 – C6	1.376(4)	N1 – V – N2	103.0(2)
N2 – C13	1.483(4)	N1 – V – C18	98.54(15)
N2 – C16	1.482(4)	N2 – V – C18	96.68(16)

* Cg is the centroid of the C(1) – C(5) ring

Complex **2.2**, prepared similarly to **2.3**, was obtained in good yield (84%) as reddish brown oil. It was crystallized from pentane at -30 ºC, but has a melting point well below room temperature. Its ^{1}H NMR V-Me resonance is found at δ 0.41 ppm (C_6D_5Br solvent). The compound is thermally unstable (more so than **2.3**) and gradually decomposes at ambient temperature. The thermolysis of the methyl vanadium complexes **2.3** and **2.2** will be discussed in more detail in Chapter 3.

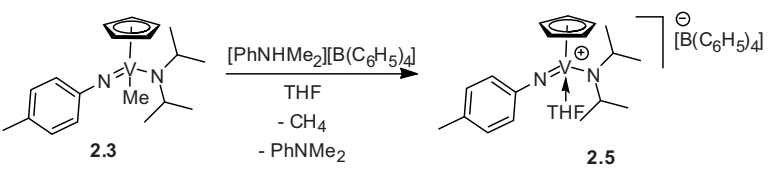
Attempts to methylate the vanadium chloride complex Cp(*t*-BuNH)V(N-*t*-Bu)Cl (**2.7**) proved to be more challenging. Preuss[33e] reported the synthesis of the Cp(*t*-BuNH)V(N-*t*-Bu)Me (**2.1**) by alkylating **2.7** with MeLi, followed by distillation at 80 – 90 ºC and 10^{-4} Torr. The procedure described by Preuss could not be reproduced by us. Following the same approach, by slow addition at 0 ºC of MeLi to a cold solution of **2.7** in hexane (1:1 ratio), followed by extraction with cold pentane, results in formation of a yellow precipitate. The ^{1}H NMR spectrum in C_6D_6 indicates the generation of a new species and the spectroscopic data are indicative for the formation of the vanadium complex CpVMe(μ-N*t*-Bu)$_2$Li(OEt$_2$) (**2.11**)[33e]. The Li salt **2.11** is pentane-soluble, and a similar behavior was reported by Horton[39] for the Li[(*t*-Bu$_3$SiN)$_2$VMe$_2$] complex. By stirring the reaction mixture, after the MeLi addition at 0 ºC, at ambient temperature for 1 h, a mixture of **2.1** and **2.11** is obtained (ratio 2:1). *Vacuum* distillation (85 ºC, 10^{-4} Torr) of the reaction mixture did not afford the Cp(*t*-BuNH)V(N-*t*-Bu)Me (**2.1**) as literature indicated, instead three resonances in the cyclopentadienyl area were recorded and a V-Me group was not observed.

Upon reaction of the chloride **2.7** with Me_2Zn at ambient temperature in hexane, followed by pentane extraction, the desired complex **2.1** could be isolated and the spectroscopic data are similar to those reported in the literature.[33] The downside of this reaction is the presence of small amounts of impurities (< 10%). Due to the high solubility of the product mixture in pentane the separation of the desired product was not achieved, even crystallization from pentane at -30 ºC did not afford pure compound **2.1**.

2.3 Generation of cationic cyclopentadienyl amido-imido vanadium(V) complexes

Early-transition metal-bound alkyl groups are in general more nucleophilic compared to those of the late transition metals and are highly reactive toward Brønsted/Lewis acids.[40,41,42] This thus provides a convenient method for generating cationic derivatives by alkyl group abstraction.

To generate stable cationic vanadium amido-imido cationic species, we initially used THF as solvent, which as a Lewis base can stabilize the Lewis acidic cation thus generated. In an NMR tube experiment, 1 equivalent of $[PhNHMe_2][B(C_6H_5)_4]$ was added to Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) in THF-d_8 at ambient temperature. The ^{1}H NMR spectrum indicated the formation of a single organometallic ionic species, $[Cp(i\text{-}Pr_2N)V(N\text{-}p\text{-tolyl})(THF\text{-}d_8)][B(C_6H_5)_4]$ (**2.5**) (Scheme 5), with the coordination of THF proven by the crystal structure of isolated **2.5** (Figure 4). There are significant differences in the ^{1}H NMR spectra of the neutral and cationic complexes. The most important are the disappearance of V-Me resonance with concomitant formation of methane (δ CH_4: 0.17 ppm in THF-d_8) and coordination of THF, which displays two multiplets at δ 3.60 and 1.75 ppm. The resonances for the cyclopentadienyl ligand (δ 6.16 ppm) and the *i*-Pr methynes (δ 5.38 / 3.90 ppm) in **2.5** are shifted significantly downfield compared to its neutral precursor **2.3** (δ 5.72 and 4.57 / 3.43 ppm for Cp and *i*-Pr CH, respectively).



2.3 **2.5**

Scheme 5

On a preparative scale, **2.5** was obtained by reacting compound **2.3** with the anilinium reagent $[PhNHMe_2][BPh_4]$ for 3 hours in THF. The cationic THF adduct **2.5** precipitates from the solution as orange needles and was obtained in 54% isolated yield. Once in the crystalline form **2.5** is practically insoluble in any common solvent at ambient temperature; only at 80 ºC gradual dissolution can be observed in THF or bromobenzene. The molecular structure (as determined by X-

ray diffraction) of **2.5** is shown in Figure 4 and a selection of bond distances and bond angles is given in Table 2.

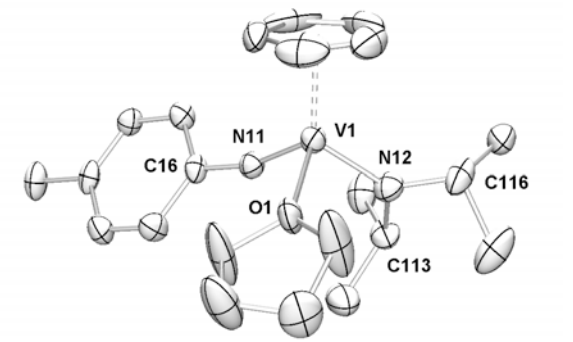


Figure 4. *Molecular structure of the cation of [Cp(i-Pr$_2$N)V(N-p-tolyl)(THF)][B(C$_6$H$_5$)$_4$] (**2.5**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.*

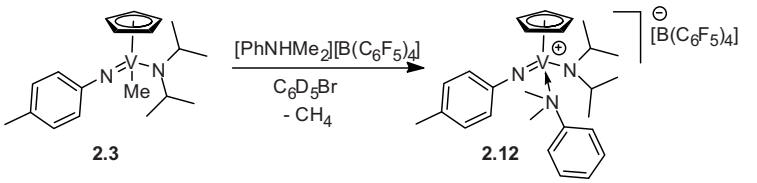
Table 2. *Selected bond lengths (Å) and angles (°) of **2.5**.*

Bond lengths	(Å)	Bond angles	(°)
V – N11	1.665(4)	V – N11 – C16	165.3(4)
V – N12	1.866(4)	V – N12 – C113	125.6(3)
V – Cg*	1.988(3)	V – N12 – C116	122.4(3)
V – O1	2.122(5)	C113 – N12 – C116	112.0(4)
N11 – C16	1.385(6)	N11 – V – N12	101.86(2)
N12 – C113	1.504(6)	N11 – V – O1	96.60(16)
N12 – C116	1.476(6)	N12 – V – O1	98.96(18)

* Cg is the centroid of the C(1) – C(5) ring

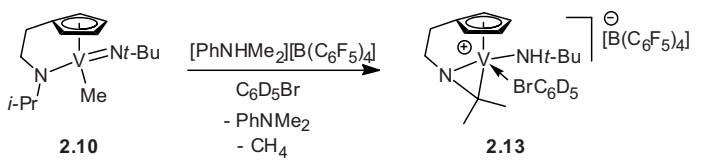
The cationic species **2.5** exhibits a typical three–legged piano stool geometry with bond distance and angles (Table 2.2) similar to compound **2.3**. Furthermore, it is clear from the X-ray structure that THF coordinates to the cationic vanadium center of **2.3**, thus blocking the vacant site created. To make the vacant site more accessible, an experiment in a less strongly coordinating solvent, C_6D_5Br, was

conducted. Reaction of **2.3** with $[PhNHMe_2][B(C_6F_5)_4]$ in C_6D_5Br generated the cationic vanadium species **2.12**. Coordination of the *N,N*-dimethylaniline to the metal in **2.12** is evident from the ^1H NMR spectrum which reveals, in addition to the number of resonances expected for the vanadium cation, two singlets for the diastereotopic methyl groups on the aniline nitrogen (δ 2.81 and 2.25 ppm) (Scheme 6).[43,44,45.]



Scheme 6

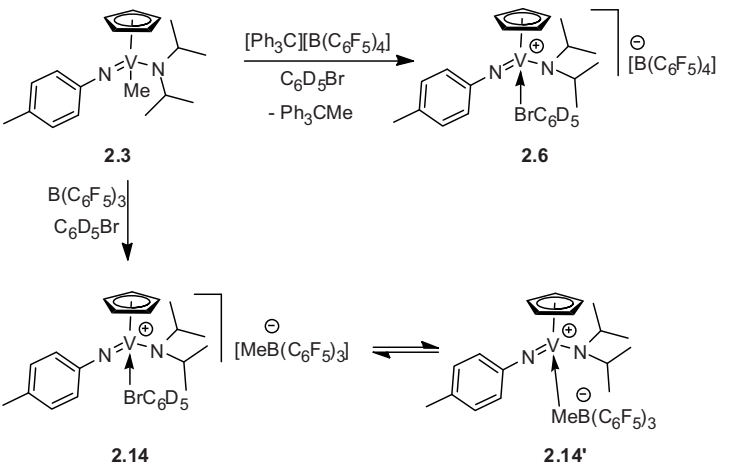
The reaction depicted above (Scheme 6) stands in marked contrast to Witte's observations on the generation of cationic vanadium complexes with a linked cyclopentadienyl-amido ligand. By treatment of the $(\eta^5\text{-}C_5H_4C_2H_4N\textit{i}\text{-Pr})V(N\text{-}\textit{t}\text{-Bu})Me$ (**2.10**) with $[PhNHMe_2][B(C_6F_5)_4]$ in C_6D_5Br, neither a bromobenzene or *N,N*-dimethylaniline adduct of an amido-imido cation were observed. Instead ^1H NMR spectroscopy indicates the formation of $[(\eta^5\text{-}C_5H_4C_2H_4N{=}CMe_2)V(NH\textit{t}\text{-Bu})][B(C_6F_5)_4]$ (**2.13**) and free *N,N*-dimethylaniline (Scheme 7).[28,29]



Scheme 7

It is remarkable that treatment of **2.3** and **2.10**[28] with the Brønsted acidic borate reagent, $[PhNHMe_2][B(C_6F_5)_4]$ leads to two completely different products. This might be explained by a higher Lewis basicity of the *t*-butyl imido ligand, relative to the *p*-tolyl imido ligand, as a result of the electron donating properties of the *t*-butyl substituent. In line with Witte's work, Nomura *et al.*[46] reported a similar reaction for $(ArN)V(N{=}C\textit{t}\text{-}Bu_2)_2Me$ (Ar = 2,6-$Me_2C_6H_3$) where the protonation of a metal-amide bond was favored over the protonation of a metal-alkyl bond.

In order to generate a more reactive cationic species, *i.e*. without $PhNMe_2$ or THF bound to the metal center, Lewis acidic borane and borate reagents were used instead. Upon treatment of $[Ph_3C][B(C_6F_5)_4]$ in an NMR tube with 1 equivalent of **2.3** in C_6D_5Br an intensely red solution formed immediately. ^1H, ^{13}C and ^{19}F NMR spectroscopic analysis confirmed the formation of the cationic vanadium complex **2.6** with the weakly-coordinating anion $[B(C_6F_5)_4]^-$ (Scheme 8).



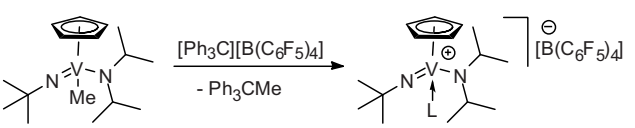
Scheme 8

The fact that the ^{19}F NMR spectrum of **2.6** shows no substantial chemical shift differences from that of $[Ph_3C]^+[B(C_6F_5)_4]^-$ at room temperature suggests that coordination of anion $B(C_6F_5)_4^-$ to vanadium centre is weak and labile.[47] According to ^1H NMR spectroscopy, the conversion to the cationic species is quantitative, with concomitant liberation of Ph_3CMe. The resonances for the Cp ligand (δ 5.72 ppm) and the *i*-Pr methynes (δ 5.11 / 3.50 ppm) in the newly formed species **2.6** are shifted considerably downfield compared to those of its neutral precursor **2.3** (δ 5.65 and 4.42 / 3.25 ppm for Cp and *i*-Pr CH, respectively). Although the coordination of bromobenzene to **2.6** has not been observed directly by spectroscopic methods, there is good precedent for it.[48] In the ^1H and ^{13}C NMR spectra the cationic species **2.6** is observed as an asymmetric structure, indicating that inversion of the metal center does not occur (on NMR time scale), probably

due to solvent stabilization. Removal of the solvent followed by washing with pentane gives the cationic species as a red foam.

Treatment of **2.3** with the Lewis acid $B(C_6F_5)_3$ also affords the related ionic species **2.14** in a straightforward manner. The **2.6** species, generated by methyl abstraction with the Lewis acid $[Ph_3C][B(C_6D_5)_4]$, has identical ^1H and ^{13}C NMR spectra with **2.14**. Evidence for C_6D_5Br stabilization of the cationic vanadium system can be seen in the ^{19}F NMR spectrum of **2.14** which indicates a 95:5 mixture of solvent separated (**2.14**) and contact ion pair (**2.14'**) species ($\Delta\delta(F_m\text{-}F_p)$ = 2.6 ppm major species; contact ion pair ($\Delta\delta(F_m\text{-}F_p)$ = 4.4 ppm minor species respectively[49]). The latter species can really be seen only in the ^{19}F NMR spectrum. Similar behavior was observed by Witte[28] for the cationic vanadium system $[(Cp\text{-amido})V(N\text{-}t\text{-}Bu)]^+$ (Figure 1 - B). Witte showed that generating the cationic species $[(Cp\text{-amido})V(N\text{-}t\text{-}Bu)]^+$ in C_6D_5Br solution, the solvent separated ion pair species ($\Delta\delta(F_m\text{-}F_p)$ = 2.4 ppm) is predominant, whereas in apolar solvent C_6D_6 predominantly is as the contact ion pair ($\Delta\delta(F_m\text{-}F_p)$ = 4.4 ppm minor).

Analogously, cationic complexes $[Cp(i\text{-}Pr_2N)V(N\text{-}t\text{-}Bu)(THF)][B(C_6F_5)_4]$ (**2.4**) and $[Cp(i\text{-}Pr_2N)V(N\text{-}t\text{-}Bu)][B(C_6F_5)_4]$ (**2.15)** were obtained on NMR spectroscopy scale experiments by methyl abstraction from compound $Cp(i\text{-}Pr_2N)V(N\text{-}t\text{-}Bu)Me$ (**2.2**) with trityl reagent $[Ph_3C][B(C_6F_5)_4]$ (Scheme 9). The latter was generated in C_6D_5Br at room temperature. The ^1H NMR and ^{13}C spectra clearly indicate the formation of a single new species after ca. 5 minutes. The disappearance of the V-Me group and formation of Ph_3CMe is indicative for the formation of **2.15**.



2.2 L = THF **2.4** C_6D_5Br **2.15**

Scheme 9

Furthermore, ^1H NMR spectra analysis reveals a small shift for the Cp ^1H resonance, but quite a large shift for the two septets of the *i*-Pr CH groups (δ 4.40 ppm and δ 3.19 ppm in the starting material to δ 5.06 ppm and δ 3.46 ppm for the new cationic species). Unfortunately, this cationic species is thermally unstable. At

room temperature, the complex **2.15** decomposes over 16 hours accompanied by the appearance of a multitude of Cp and *t*-Bu absorptions, and a disappearance of the *iso*propyl absorptions. No identifiable species could be obtained from this mixture.

When Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) was treated with [$PhNHMe_2$][$B(C_6F_5)_4$] in C_6D_5Br at room temperature gas evolution was observed immediately. Unfortunately, the ^{1}H NMR spectrum showed the formation of multiple products (up to 10 resonances in the cyclopentadienyl area) which could not be identified, rendering this synthesis route for the formation of cationic species like **2.4** inaccessible. [50]

2.4 Concluding remarks

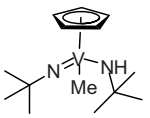
Half-sandwich (*p*-tolylimido) vanadium(V) complexes are most conveniently synthesized starting from (*i*-Pr_2N)V(N-*p*-tolyl)Cl_2 by introduction of the Cp ligand, whereas the half-sandwich (*t*-Bu-imido) vanadium(V) complexes can be synthesized either by introducing first the Cp ligand or the amido ligand to Cl_3V(N*t*-Bu). The neutral half-sandwich (*p*-tolylimido) vanadium(V) amido methyl complex shows a different reactivity towards the Brønsted acid $[PhNMe_2H]^+$ than the linked (η^5-$C_5H_4C_2H_4$N*i*-Pr)V(N-*t*-Bu)Me system. Whereas the latter undergoes protonation of the imido ligand, the former undergoes direct protonation of the V-Me group, possibly due to higher Lewis basicity of the *t*-butyl imido ligand relative to the *p*-tolyl imido ligand. The choice of activator can have an important effect on the nature of the generated unsaturated vanadium system. The presence of a Lewis base such as THF or $PhNMe_2$ stabilizes the unsaturated vanadium amido-imido cationic center, and such stabilization might diminish catalytic activity. A 'naked' (weakly solvated) cationic species could be obtained using Lewis acids [Ph_3C][$B(C_6F_5)_4$] and $B(C_6F_5)_3$ in bromobenzene solvent. When the Lewis acid $B(C_6F_5)_3$ was used, the cationic species generated was observed as a mixture of the solvent separated and the contact ion pair in solution (bromobenzene-d_5, 95:5, respectively). The possibility of generating these cationic species may provide an entry into probing their catalytic activity.

2.5 Experimental section

General considerations. The experiments described were performed under a dinitrogen atmosphere using standard Schlenk, vacuum line, and glove-box techniques. Solvents (Aldrich, anhydrous) were passed over a column containing BASF R_3-11 supported Cu based scavenger and either a mixture of alumina and 3Å mol sieves (toluene), 4Å mol sieves (pentane, hexane) or alumina (THF, diethyl ether) under a dinitrogen atmosphere before use. The deuterated solvents THF-d_8, C_6D_6, $C_6D_5CD_3$ (Aldrich) were dried on Na/K alloy and vacuum transfered prior use, CD_2Cl_2 and C_6D_5Br were dried on CaH_2 and vacuum transfer before use. The reagent MeLi (1.6 M in diethyl ether, Aldrich) was used as received. N,N-Dimethylaniliniumborate $[PhNHMe_2][B(C_6F_5)_4]$ (Strem), trityl borate $[Ph_3C][B(C_6F_5)_4]$ (Strem), $OVCl_3$ (Aldrich), *p*-tolylNCO (Aldrich) were used as received. $B(C_6F_5)_3$[51] and $[PhNHMe_2][B(C_6H_5)_4]$[52] were synthesized according to literature procedures. *p*-Toluidine (Aldrich) was sublimed prior to use, and *i*-Pr_2NH and *t*-$BuNH_2$ (Acros) were dried on CaH_2 and vacuum transferred before use. The following compounds were prepared according to the literature procedures: Cp(*t*-BuNH)V(N-*t*-Bu)Cl (**2.7**)[33e], Cl_3V(N-*p*-tolyl) [32], (*i*-Pr_2N)V(N-*p*-tolyl)Cl_2[28], Cp(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**2.9**)[28], Cl_3V(N-*t*-Bu),[33d] (*i*-Pr_2N)V(N-*t*-Bu)Cl_2[33g], Cp(*i*-Pr_2N)V(N-*t*-Bu)Cl (**2.8**)[33g].

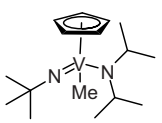
All ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian VXR-300 (300 MHz), Varian Mercury Plus (400 MHz) or Unity (500 MHz) spectrometers on samples prepared in an NMR tube equipped with Teflon (Young) valve. Chemical shifts were determined relative to the residual solvent peaks for ^{1}H NMR (CD_2Cl_2, δ = 5.32 ppm; C_6D_6, δ = 7.15 ppm; THF-d_8, δ = 3.57, 1.72 ppm; C_6D_5Br, δ = 7.30, 7.02, 6.95 ppm) and for ^{13}C NMR (C_6D_6, δ = 128 ppm; C_6D_5Br, δ = 130.93, 129.39, 126.23, 122.17; CD_2Cl_2, δ = 53.80 ppm; THF-d_8, δ = 68.40 ppm, 26.26 ppm). ^{51}V NMR chemical shifts are reported in ppm relative to $VOCl_3$ which is used as an external reference ($VOCl_3$, δ = 0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad and m = multiplet), coupling constants and integration. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Synthesis of Cp(*t*-BuNH)V(N*t*-Bu)Me (2.1)



A solution Me_2Zn (1.09 mmol, 0.10 g, 2M in toluene) was slowly added to a solution of **2.7** (1.82 mmol, 0.50 g) in pentane at room temperature. The reaction mixture was stirred for 5 h and the color changed from orange to dark red (formation of $ZnCl_2$ precipitate is observed). All volatiles were removed *in vacuo* and the resulting residue was extracted with pentane (10 mL). The solvent was pumped off providing a red-brown oil (<10 % impurities). ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 9.22 (s, 1H NH), 5.52 (s, 5H Cp), 1.34 (s, 9H *t*-BuNH), 1.21 (s, 9H *t*-BuN), 0.78 (s, 3H V-Me). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ºC): δ 105.54 (*C*H Cp), 31.27 (*C*H$_3$ *t*-Bu), 30.85 (*C*H$_3$ *t*-Bu), V-Me not observed.

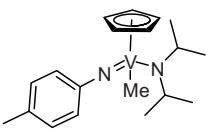
Synthesis of Cp(*i*-Pr$_2$N)V(N-*t*-Bu)Me (2.2)



To a cold (-40 ºC) solution of Cp(*i*-Pr$_2$N)V(N*t*-Bu)Cl (**2.8**) (7.16 g, 22.18 mmol) in diethyl ether (150 mL), MeLi (14 mL, 1.6M, 22.18 mmol) was added dropwise. The mixture was warmed up to -10 ºC and stirred for 1 hour. The color of the solution changed from red to yellow-brown. The work up was carried out at -10 ºC. After removal of the solvent *in vacuo*, the residual ether was stripped off by addition of 2 x 20 mL of cold pentane and subsequent removal of the volatiles *in vacuo*. Extraction of the reaction mixture with 100 mL cold pentane and removal of the solvent *in vacuo* at -10 ºC yielded 5.65 g (18.69 mmol, 84 %) of **2.2** as a brown oil, which crystallizes at around -30 ºC. ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 5.66 (5H Cp), 4.40 (sept, J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 3.19 (m, 1H CH *i*-Pr), 1.65 (d, J_{HH} = 6.4 Hz, 3H CH$_3$ *i*-Pr), 1.24 (s, 9H CH$_3$ *t*-Bu), 1.33 (d, J_{HH}= 6.5 Hz, 3H CH$_3$ *i*-Pr), 0.90 (d, J_{HH} = 6.5 Hz, 3H CH$_3$ *i*-Pr), 0.83 (d, J_{HH} = 6.6 Hz, 3H CH$_3$ *i*-Pr), 0.41 (s broad, 3H V-Me). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 ºC): δ 104.93 (*C*H Cp), 62.03 (*C*H, *i*-Pr), 52.90 (*C*H, *i*-Pr), 32.36 (*C*H$_3$, *i*-Pr), 31.76 (*C*H$_3$, *t*-Bu), 27.09 (*C*H$_3$, *i*-Pr), 20.41 (*C*H$_3$, *i*-Pr), 19.38 (*C*H$_3$, *i*-Pr), C$_q$ of *t*-Bu and V-Me not observed. ^{51}V NMR (131 MHz, C_6D_6, 25 ºC, $VOCl_3$ external standard): δ -667.98 (t, J_{VN} = 86.60 Hz). ^{1}H NMR (400 MHz, THF-d$_8$, 25 ºC): δ 5.71 (s, 5H Cp), 4.52 (sept, J_{HH} = 6.2 Hz, 1H, CH *i*-Pr), 3.34 (broad, 1H, CH *i*-Pr), 1.64 (d, J_{HH} = 6.1 Hz, 3H CH$_3$ *i*-Pr), 1.36 (d, J_{HH} = 6.3 Hz, 3H CH$_3$ *i*-Pr), 1.02 (d, J_{HH} = 6.2 Hz, 3H CH$_3$ *i*-Pr), 0.86 (d, J_{HH} = 6.3

Hz, 3H CH_3 *i*-Pr), 1.31 (s, 9H CH_3 *t*-Bu), 0.21 (s, 3H V-Me). ^{13}C {^1H} NMR (100 MHz, THF-d_8, 25 ºC): δ 106.36 (*C*H Cp), 63.87 (*C*H, *i*-Pr), 54.07 (*C*H, *i*-Pr), 33.52 (*C*H_3, *i*-Pr), 32.95 (*C*H_3, *t*-Bu), 28.27 (*C*H_3 *i*-Pr), 24.81 (*C*H_3 *i*-Pr), 21.62 (*C*H_3, *i*-Pr), C_q of *t*-Bu and V-Me not observed. ^{51}V NMR (131 MHz, THF-d_8, 25 ºC, $VOCl_3$ external standard): δ -671.93 (t, J_{VN} = 81.82 Hz).

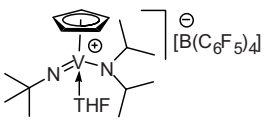
Synthesis of Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (2.3)



A solution of MeLi (2.16 mL, 1.6 M in ether, 3.31 mmol) was added to a cooled (-40 ºC) solution of 1.18 g (3.31 mmol) of Cp(*i*-Pr_2N)V(N*p*-tolyl)Cl (**2.9**) in 50 mL of ether. The reaction mixture was stirred for 20 minutes at -10 ºC and the color of the solution changed from red to orange. All volatiles were removed *in vacuo* and the resulting solid was stripped of residual ether by stirring with 2 portions of cold pentane and subsequent removal *in vacuo* at -10 ºC. Extraction with 30 mL of cold pentane and removal of the solvent *in vacuo* at -10 ºC yielded 0.81 g (2.41 mmol, 73 %) of Cp(*i*-Pr_2N)V(N*p*-tolyl)Me as greenish brown powder. Recrystallization from pentane gave brown red block-shaped crystals suitable for X-ray diffraction. ^1H NMR (400 MHz, THF-d_8, 25 ºC): δ 7.00 (d, J_{HH} = 8.8 Hz, 2H C*H* *p*-tolylN), 6.94 (d, J_{HH} = 8.8 Hz, 2H C*H* *p*-tolylN), 5.72 (s, 5H Cp), 4.57 (sept, J_{HH} = 6.4 Hz, 1H C*H* *i*-Pr), 3.43 (br, 1H C*H* *i*-Pr), 2.28 (s, 3H CH_3 *p*-tolylN), 1.62 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr), 1.40 (d, J_{HH} = 6.60 Hz, 3H, CH_3 *i*-Pr), 1.08 (d, J_{HH} = 6.60 Hz, 3H CH_3 *i*-Pr), 0.92 (d, J_{HH} = 6.60 Hz, 3H CH_3 *i*-Pr), 0.40 (s, CH_3 – V). ^{13}C {^1H} NMR (100 MHz, C_6D_6 , 25 ºC): δ 135.23 (*ipso*-C *p*-tolylN), 130.50 (*C*H *p*-tolylN), 126.20 (*C*H *p*-tolylN), 107.60 (*C*H Cp), 63.43 (*C*H *i*-Pr), 56.35 (*C*H *i*-Pr), 33.29 (*C*H_3 *i*-Pr), 28.24 (*C*H_3 *i*-Pr), 22.18 (*C*H_3 *p*-tolylN), 21.82 (*C*H_3 *i*-Pr), 20.31 (*C*H_3 *i*-Pr), V-Me not observed. ^1H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 7.06 (d, J_{HH} = 7.9 Hz, 2H CH *p*-tolylN), 6.88 (d, J_{HH} = 8.0 Hz, 2H CH *p*-tolylN), 5.65 (5H Cp), 4.42 (sept, J_{HH} = 6.5 Hz, 1H, CH *i*-Pr), 3.25 (q, , J_{HH} = 6.2 Hz, 1H, CH *i*-Pr), 2.18 (s, 3H, Me *p*-tolylN), 1.68 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.38 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 0.93 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.87 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 0.62 (s broad, CH_3–V). ^{13}C {^1H}NMR (100 MHz, C_6D_5Br, 25ºC): δ 133.12 (*C* *ipso*, *p*-tolylN), 128.78 (*C*H, *p*-tolylN), 124.42 (*C*H *p*-tolylN), 105.57 (*C*H Cp), 61.42 (*C*H *i*-Pr), 54.45 (*C*H *i*-Pr), 31.88 (*C*H_3 *i*-Pr), 26.74 (*C*H_3 *i*-Pr), 21.06 (*C*H_3 *p*-tolylN), 20.33 (*C*H_3 *i*-Pr), 18.86(*C*H_3 *i*-Pr). ^{51}V NMR (131 MHz, C_6D_6, 25 ºC,

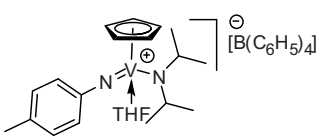
$VOCl_3$ external standard): δ -600 ($\Delta_{1/2}$ = 320 Hz). Anal. Calcd.(%) for $C_{19}H_{29}N_2V$: C, 67.84; H, 8.69; N, 8.33. Found: C, 67.75; H, 9.03; N, 8.29.

Generation of [Cp(*i*-Pr$_2$N)V(N*t*-Bu)(THF-d_8)][B(C$_6$F$_5$)$_4$] (2.4)



Cationic species **2.4** was generated quantitatively in situ by the treatment of **2.2** (0.02 g, 0.06 mmol) with $[Ph_3C][B(C_6F_5)_4]$ (0.05 g, 0.06 mmol) in THF-d_8 (0.5 mL) at ambient temperature. The solution immediately changed from red-brown to wine-red. The NMR spectra indicated full conversion to the cationic species **2.4** with concomitant formation of Ph_3CMe. ^{1}H NMR (400 MHz, THF-d_8, 25 ºC): δ 7.29 ~ 7.03 (m, 15H Ph_3CMe), 6.37 (s, 5H Cp), 5.48 (sept, J_{HH} = 5.8 Hz, 1H CH *i*-Pr), 3.90 (sept, J_{HH} = 5.8 Hz, 1H CH *i*-Pr), 2.15 (s, 3H CH_3 Ph_3CMe), 1.86 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.53 (s, 9H CH_3 *t*-Bu), 1.38 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.29 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.13 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, THF-d_8, 25 ºC): δ 151.08 (*ipso-C* Ph_3CMe), 150.18 (d, J_{CF} = 239.9 Hz, *o*-CF B(C_6F_5)$_4$), 140.36 (d, J_{CF} = 198.8 Hz, *p*-CF B(C_6F_5)$_4$), 137.94 (d, J_{CF} = 204.1 Hz, *m*-CF B(C_6F_5)$_4$), 131.19 (*C*H, Ph_3CMe), 129.92 (*C*H, Ph_3CMe), 127.90 (*C*H, Ph_3CMe), 126.26 (broad *ipso-C* B(C_6F_5)$_4$), 110.91 (*C*H Cp), 70.66 (*C*H, *i*-Pr), 64.57 (C, *t*-Bu), 60.87 (*C*H, *i*-Pr), 45.65 (C, Ph_3CMe), 33.29 (CH_3, Ph_3C*Me*), 33.11 (CH_3, *t*-Bu), 31.84 (CH_3, *i*-Pr), 29.14 (CH_3, *i*-Pr), 23.63 (CH_3, *i*-Pr), 21.99 (CH_3, *i*-Pr). ^{19}F {^{1}H} NMR (100 MHz, THF-d_8, 25 ºC): δ – 133.05 (s, *o*-F B(C_6F_5)$_4$), - 165.16 (t, J_{CF} = 18.9, *p*-F B(C_6F_5)$_4$), - 168.62 (s, *m*-F, B(C_6F_5)$_4$). ^{51}V NMR (131 MHz, THF-d_8, 25 ºC, $VOCl_3$ external standard): δ -533.26 ($\Delta_{1/2}$ = 1730 Hz).

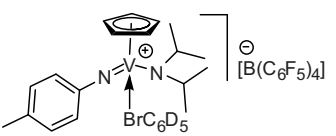
Synthesis of [Cp(*i*-Pr$_2$N)V(N*p*-tolyl)(THF)][B(C$_6$F$_5$)$_4$] (2.5)



To a mixture of Cp(*i*-Pr$_2$N)V(N*p*-tolyl)Me (**2.3**) (0.20 g, 0.60 mmol) and $[PhNMe_2H][BPh_4]$ (0.40 g, 0.91 mmol), 5 mL of THF was added. After 3 h the THF was evaporated under reduced pressure, and the crude product was washed with 2 portions of 3 mL of pentane. The reaction mixture was dissolved again in 5 mL of THF, and warmed to 80 ºC. Cooling to room temperature yielded product **3c** as orange needles 0.23 g (0.32 mmol, 54 %).

^{1}H NMR (400 MHz, THF-d_8, 25 ºC): δ 7.33 ~ 7.29 (broad m, 8H *o*-CH B*Ph*$_4$), 7.22 (d, J_{HH} = 8.4 Hz, 2H, *p*-tolylN), 7.15 (d, J_{HH} = 8.4 Hz, 2H *p*-tolylN), 6.86 (t, J_{HH} = 7.4 Hz, 8H *m*-CH B*Ph*$_4$), 6.71 (t, J_{HH} = 7.0 Hz, 4H *p*-CH B*Ph*$_4$), 6.18 (s, 5H, Cp), 5.38 (sept, J_{HH} = 6.3 Hz, 1H, C*H* *i*-Pr), 3.90 (sept, J_{HH} = 6.3 Hz, 1H, C*H* *i*-Pr), 2.38 (s, 3H C*H*$_3$ *p*-tolyl), 1.83 (d, J_{HH} = 6.2 Hz, 3H, C*H*$_3$ *i*-Pr), 1.34 (d, J_{HH} = 6.6 Hz, 3H C*H*$_3$ *i*-Pr), 1.28 (d, J_{HH} = 6.2 Hz, 3H C*H*$_3$ *i*-Pr), 1.10 (d, J_{HH} = 6.6 Hz, 3H C*H*$_3$ *i*-Pr). ^{13}C {^{1}H} NMR (100 MHz, THF-d_8, 25 ºC): δ 166.40 (q, J_{CB}= 49.56, C, PhB), 140.90 (*ipso*-C, *p*-tolyl), 138.31 (CH, PhB), 131.4 (CH, *p*-tolylN), 127.5 (CH, *p*-tolylN), 126.7 (CH, PhB), 122.9 (CH, PhB), 118.1 (*ipso*-C, *p*-tolylN), 112.24 (*C*H Cp), 70.04 (*C*H, *i*-Pr), 67.42 (OC*H*$_2$, THF), 60.95 (*C*H, *i*-Pr), 31.24 (*C*H$_3$, *i*-Pr), 27.4 (*C*H$_3$, *i*-Pr), 25.6 (*C*H$_2$, THF), 21.88 (*C*H$_3$, *i*-Pr), 20.52 (*C*H$_3$, *p*-tolylN), 20.26 (*C*H$_3$, *i*-Pr). Anal.Calcd. (%) for $C_{46}H_{54}N_2BOV$: C, 77.45; H, 7.52; N, 3.92. Found: C, 77.58; H, 7.48; N, 3.77. ^{51}V NMR (131 MHz, THF-d_8, 25 ºC, $VOCl_3$ external standard): δ -442.35 ($\Delta_{1/2}$ = 3675 Hz).

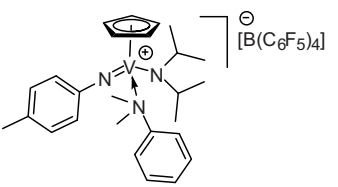
Generation of [Cp(*i*-Pr$_2$N)V(N*p*-tolyl)][B(C$_6$F$_5$)$_4$] (2.6)



The cationic vanadium(V) complex [Cp(*i*-Pr$_2$N)V(N*p*-tolyl)][B(C$_6$F$_5$)$_4$] (**2.6**) was generated by adding [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.03 g, 0.03 mmol) to a solution of Cp(*i*-Pr$_2$N)V(N*p*-tolyl)Me (**2.3**) (0.01 g, 0.03 mmol) in C$_6$D$_5$Br (0.6 mL), resulting in immediate color change to cherry red. According to NMR spectroscopic data, the conversion to the cationic species **2.6** is quantitative, with concomitant liberation of Ph$_3$CMe. Removal of the solvent *in vacuo* gives the ionic species as a red oil. ^{1}H NMR (400 MHz, C$_6$D$_5$Br, 25 ºC): δ 7.16 ~ 7.04 (m, 15H *Ph*$_3$CMe), 6.92 (s broad, 4H *p*-tolylN), 5.72 (s, 5H, Cp), 5.11 (sept, J_{HH} = 6.6 Hz, 1H, C*H* *i*-Pr), 3.50 (sept, J_{HH} = 6.6 Hz, 1H, C*H* *i*-Pr), 2.19 (s, 3H C*H*$_3$ *p*-tolyl), 2.04 (s, 3H C*H*$_3$ Ph$_3$C*Me*), 1.51 (d, J_{HH} = 6.4 Hz, 3H C*H*$_3$ *i*-Pr), 1.13 (d, J_{HH} = 6.4 Hz, 3H, C*H*$_3$ *i*-Pr), 0.92 (d, J_{HH} = 6.4 Hz, 3H, CH$_3$ *i*-Pr), 0.85 (d, J_{HH} = 6.5 Hz, 3H, CH$_3$ *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, C$_6$D$_5$Br, 25 ºC): δ 148.91 (*ipso-C Ph*$_3$CMe), 148.47 (d, J_{CF} = 238.6 Hz, *o*-CF B(*C*$_6$F$_5$)$_4$), 140.01 (*ipso-C p*-tolylN), 138.27 (d, J_{CF} = 237.9 Hz, *p*-CF B(*C*$_6$F$_5$)$_4$), 136.44 (d, J_{CF} = 242.4 Hz, *m*-CF B(*C*$_6$F$_5$)$_4$), 129.60(CH, *p*-tolylN overlap with the solvent), 128.65 (*C*H, *Ph*$_3$CMe), 127.80 (*C*H, *Ph*$_3$CMe), 125.87 (*C*H, *Ph*$_3$CMe), 125.33 (*C*H, *p*-tolylN), 110.00 (*C*H, Cp), 70.15 (*C*H, *i*-Pr), 62.14 (*C*H, *i*-Pr), 52.38 (C, Ph$_3$*C*Me), 32.17 (*C*H$_3$, *i*-Pr), 30.36 (*C*H$_3$, Ph$_3$C*Me*), 26.67 (*C*H$_3$, *i*-Pr), 21.20 (*C*H$_3$, *i*-Pr), 20.18

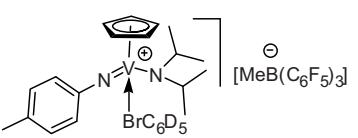
(*C*H_3, *p*-tolylN), 20.16 (*C*H_3, *i*-Pr), *ipso*-C B(C_6F_5)$_4$ not observed. Assignments were aided by ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments. ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ – 132.19 (s, *o*-F B(C_6F_5)$_4$), - 162.44 (t, J = 20.8 Hz, *p*-F B(C_6F_5)$_4$), - 166.32 (t, J = 18.4 Hz, m-F, B(C_6F_5)$_4$). ^{51}V NMR (131 MHz, C_6D_5Br, 25 ºC, $VOCl_3$ external standard): δ -393.99 ($\Delta_{1/2}$ = 3385 Hz).

Generation of [Cp(*i*-Pr_2N)V(N*p*-tolyl)(PhNMe_2)][B(C_6F_5)$_4$] (2.12)



[PhNHMe_2][B(C_6F_5)$_4$] was added (0.05 g, 0.06 mmol) to a solution of Cp(*i*-Pr_2N)V(N*p*-tolyl)Me (**2.3**) (0.02 g, 0.06 mmol) in C_6D_5Br (0.5 mL) at room temperature. Gas evolution was observed and the color of the solution had turned from red-brownish to intense red. NMR analysis showed clean conversion to **2.12**. ^{1}H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 7.19 ~7.0 (m, 5H CH PhNMe_2 and 2H CH *p*-tolylN, overlap with solvent), 6.89 (d, J_{HH} = 7.8 Hz, 2H, CH *p*-tolylN), 5.34 (5H Cp), 4.88 (sept, J_{HH} = 6.0 Hz, 1H CH *i*-Pr), 3.52 (sept, J_{HH} = 6.2 Hz 1H, CH *i*-Pr), 2.81 (s, 3H PhN*M*e_2), 2.56 (s, 3H CH_3 *p*-tolylN), 2.25 (s, 3H PhN*M*e_2), 1.78 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.98 (d, J_{HH} = 6.1 Hz, 6H CH_3 *i*-Pr), 0.93 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr). ^{13}C{^{1}H} NMR (C_6D_5Br, 25 ºC) δ 151.5 (*ipso*-C, *p*-tolylN), 148.7 (d, J_{CF} = 241 Hz, B(C_6F_5)$_4$), 139.8 (*ipso*-C, *p*-tolylN), 135.7 (t, J_{CF} = 238 Hz, B(C_6F_5)$_4$), 130.0, 127.0, 125.9 (*C*H *p*-tolylN and *Ph*NMe_2), 119.5 (*C*H *p*-tolylN), 110.0 (*C*H Cp), 68.7 (*C*H *i*-Pr), 61.5 (*C*H *i*-Pr), 58.5 (PhN*M*e_2), 50.0 (PhN*M*e_2), 32.1 (*C*H_3 *i*-Pr), 26.5 (*C*H_3 *i*-Pr), 21.4 (*C*H_3 *p*-tolylN), 21.3 (*C*H_3 *i*-Pr), 20.6 (*C*H_3 *i*-Pr). ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ -132.3 (*o*-F), -162.4 (t, 21 Hz, *p*-F), -166.3 (*m*-F).

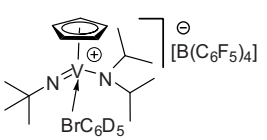
Generation of [Cp(*i*-Pr_2N)V(N*p*-tolyl)][MeB(C_6F_5)$_3$] (2.14)



B(C_6F_5)$_3$ (0.04 g, 0.07 mmol) was added to a solution of Cp(*i*-Pr_2N)V(N*p*-tolyl)Me (**2.3**) (0.02 g, 0.07 mmol) in C_6D_5Br (0.6 mL). The ^{1}H NMR spectrum showed full conversion to **2.14**. The formation of cationic species was accompanied by a color change from red-brown to intense red. ^{19}F NMR analysis showed the presence of a small amount of the

contact ion pair (< 5%). ^{1}H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 6.92 (m, 4H *p*-tolylN), 5.72 (s, 5H Cp), 5.11 (sept, J_{HH} = 6.6 Hz, 1H C*H* *i*-Pr), 3.50 (sept, J_{HH} = 6.2 Hz, 1H C*H* *i*-Pr), 2.19 (s, 3H CH_3 *p*-tolylN), 1.51 (d, J_{HH} = 6.4 Hz, 3H *i*-Pr), 1.15 (s broad, 3H Me), 1.12 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr), 0.92 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 0.84 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, C_6D_5Br, 25ºC): δ 148.67 (d, J_{CF} = 240.8 Hz, *o*-CF B(C_6F_5)$_3$), 139.98 (*ipso*-C *p*-tolylN), 137.42 (d, J_{CF} = 249.2 Hz, *p*-CF B(C_6F_5)$_3$), 136.57 (d, J_{CF} = 246.1 Hz, *m*-CF B(C_6F_5)$_3$), 129.60 (CH, *p*-tolylN overlap with the solvent), 125.34 (*C*H, *p*-tolylN), 110.058 (*C*H Cp), 70.18 (*C*H, *i*-Pr), 62.16 (*C*H, *i*-Pr), 32.19 (*C*H_3, *i*-Pr), 26.69 (*C*H_3, *i*-Pr), 21.19 (*C*H_3, *i*-Pr), 20.21 (*C*H_3, *p*-tolylN), 20.19 (*C*H_3, *i*-Pr), 11.02 (br, B-Me).^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ -132.49 (d, *J* = 21.4 Hz, *o*-F B(C_6F_5)$_3$), -132.82* (*o*-F), -160.26* (*p*-F), -164.06 (t, *J* = 21.0 Hz, *p*-F B(C_6F_5)$_3$), -164.71* (*m*-F), -166.61 (t, *J* = 19.7 Hz, *m*-F B(C_6F_5)$_3$). Resonances marked with an asterisk are from the contact ion-pair (< 5%).

Generation of [Cp(*i*-Pr$_2$N)V(N*t*-Bu)][B(C_6F_5)$_4$] (2.15)



[Ph_3C][B(C_6F_5)$_4$] (0.03 g, 0.03 mmol) was added in an NMR tube to a solution of **2.2** (0.01 g, 0.03 mmol) in C_6D_5Br (0.5 mL) at ambient temperature. The NMR spectra indicated quantitative formation of **2.15** with concomitant formation of Ph_3CMe. The formation of **2.15** was accompanied by a color change from red-brown to intense red. The compound is thermally not very stable, and gradually decomposes over 16 h at ambient temperature. ^{1}H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 7.16 ~ 7.06 (m, 15H Ph_3CMe), 5.68 (s, 5H Cp), 5.06 (sept, J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 3.46 (sept, J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 2.04 (s, 3H CH_3 Ph_3CMe), 1.51 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.11 (s, 9H CH_3 *t*-Bu), 1.05 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.86 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 0.80 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, C_6D_5Br, 25 ºC): δ 149.13 (*ipso-C* *Ph*$_3$CMe), 148.72 (d, J_{CF} = 244.2 Hz, *o*-CF B(C_6F_5)$_4$), 138.81 (d, J_{CF} = 187.9 Hz, *p*-CF B(C_6F_5)$_4$), 136.39 (d, J_{CF} = 188.8 Hz, *m*-CF B(C_6F_5)$_4$), 128.85 (*C*H, *Ph*$_3$CMe), 128.00 (*C*H, *Ph*$_3$CMe), 126.07 (*C*H, *Ph*$_3$CMe), 124.60 (broad *ipso-C* B(C_6F_5)$_4$), 109.16 (*C*H Cp), 71.02 (*C*H, *i*-Pr), 62.79 (C, *t*-Bu), 60.99 (*C*H, *i*-Pr), 43.81 (C, Ph_3*C*Me), 32.52 (*C*H_3, *i*-Pr), 31.18 (*C*H_3, Ph_3CMe), 30.56 (*C*H_3, *t*-Bu), 27.03 (*C*H_3, *i*-Pr), 20.53 (*C*H_3, *i*-Pr), 20.36 (*C*H_3, *i*-Pr). ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ – 133.02 (s, *o*-F B(C_6F_5)$_4$), - 163.08 (s, *p*-F B(C_6F_5)$_4$), - 166.66 (s, *m*-F,

$B(C_6F_5)_4$). ^{51}V NMR (131 MHz, C_6D_5Br, 25 ºC, $VOCl_3$ external standard): δ -487.63 ($\Delta_{1/2}$ = 3750) Hz.

X-ray crystal structure determinations. Suitable crystals of **2.3** and **2.5** were mounted on top of a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream on a Bruker22 SMART APEX CCD diffractometer.

The final unit cell was obtained from the xyz centroids of 4615 (**2.3**) and 3813 (**2.5**) reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).[53] The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF[54] A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined. All refinement and geometry calculations were performed with the program packages *SHELXL*[55] and *PLATON.*[56] Crystal data and details on data collection and refinement are presented in Table 3.

Table 3. Crystallographic data for **2.3** and **2.5**.

	2.3	***2.5***
chem formula	$C_{19}H_{29}N_2V$	$[C_{22}H_{34}N_2OV]^+$ $[C_{24}H_{20}B]^-$
Fw	336.39	712.70
crystal system	monoclinic	triclinic
color, habit	brown, block	red, block
size, mm	0.19 x 0.16 x 0.13	0.26 x 0.21 x 0.16
space group	$P2_1/c$	P-1
a, Å	13.380(1)	9.2873(9)
b, Å	11.0573(9)	12.827(1)
c, Å	13.949(1)	16.830(2)
α, (°)	-	93.630(2)
β, (°)	116.596(1)	94.974(2)
γ, (°)	-	104.100(1)
V, Å^3	1845.3(2)	1929.8(3)
Z	1	1
ρ_{calc}, g.cm^{-3}	1.211	1.226
F(000)	720	760
μ(Mo K$\overline{\alpha}$), cm^{-1}	5.37	2.94
temperature (K)	100(1)	100(1)
θ range (°)	2.51 – 26.73	2.44 – 25.03
min and max transm	0.8176 – 0.9335	0.8591 – 0.9544
R(F)	0.0525	0.0823
wR(F^2)	0.1292	0.2313
GooF	1.030	1.022
observed reflns $F_o \geq 4.0\ \sigma\ (F_o)$)	2797	4562
data collected (h, k, l)	-15:16; -13:13; -17:17	-11:11; -15:15; -20:19
params refined	288	465

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[50] ^{1}H NMR spectrum showed the presence of free $PhNMe_2$: ^{1}H NMR (400 MHz, C_6D_5Br, 25 °C): δ 7.16 (t, J_{HH} = 7.4 Hz, 2H *Ph*NMe_2), 6.82 (t, J_{HH} = 6.8 Hz, 1H *Ph*NMe_2), 6.60 (t, J_{HH} = 7.9 Hz, 2H *Ph*NMe_2), 2.57 (s, 6H, PhN*Me*$_2$); Otten, E. *Versatile coordination behaviour of cyclopentadienyl-arene ligands on early transition metals*, PhD-Thesis, Groningen, **2008**.

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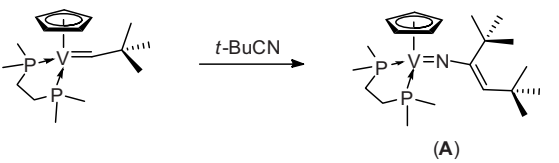
Chapter 3

Generation of low valent vanadium CpV(III)-imido species

*The thermal stability of cyclopentadienyl vanadium-methyl complexes (η^5-C_5H_5)(i-Pr_2N)V(N-t-Bu)Me (**2.2**) and (η^5-C_5H_5)(i-Pr_2N)V(N-p-tolyl)Me (**2.3**) was investigated, providing a new route to the generation of CpV(III)-imido species. These CpV(III)-imido moieties generated during the thermolysis process could be trapped by performing the decomposition reaction in the presence of the phosphines PMe_3 and dmpe. In the presence of suitable reagents these low valent vanadium (III) species can perform oxidative addition reactions to give vanadium(V).*

3.1 Introduction

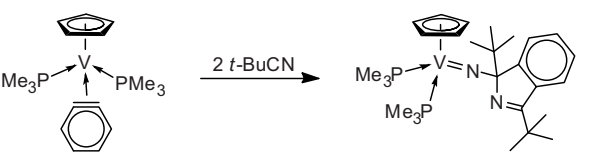
Although vanadium(V) imido complexes have been investigated extensively, [1,2,3] much less is known about imido complexes of vanadium(III). The first example of a V(III) d^2 imido complex was obtained by Hessen *et al.*[4] from the reaction of the V(III) alkylidene CpV(dmpe)=C(H)*t*-Bu with *t*-BuCN to yield CpV(dmpe)=NC*t*-Bu=C(H)*t*-Bu (**A**) (Scheme 1).



Scheme 1

Buijink[5] and Preuss and coworkers[6] used d^0 half-sandwich imido vanadium dichloride complexes as precursors to generate d^2 vanadium(III) cyclopentadienyl imido species through reductive dehalogenation with magnesium. By treatment of $CpV(NAr)Cl_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) with magnesium in THF in the presence of trimethylphosphine or trimethylphosphite Buijink[5] prepared $CpV(NAr)(PMe_3)_2$ and $CpV(NAr)(P(OMe)_3)_2$ respectively. Preuss and coworkers[6] generated a series of imidovanadium(III) complexes [$CpV(N\text{-}t\text{-}Bu)(PR_3)_2$, ($PR_3$ = PMe_3, PEt_3, P*n*-Bu_3, PMe_2Ph, $PMePh_2$, $P(OMe)_3$, $P(OPh)_3$); $CpV(N\text{-}t\text{-}Bu)(CO)_2$ and $CpV(N\text{-}t\text{-}Bu)(PMe_3)(CO)$] starting from $CpV(N\text{-}t\text{-}Bu)Cl_2$.

A more exotic route to a V(III) imido species is the reaction of the V(III) benzyne complex $CpV(\eta^2\text{-}C_6H_4)(PMe_3)_2$ with 2 equiv *t*-BuCN to yield the half-sandwich vanadium(III)-imido compound shown in Scheme 2.[5]

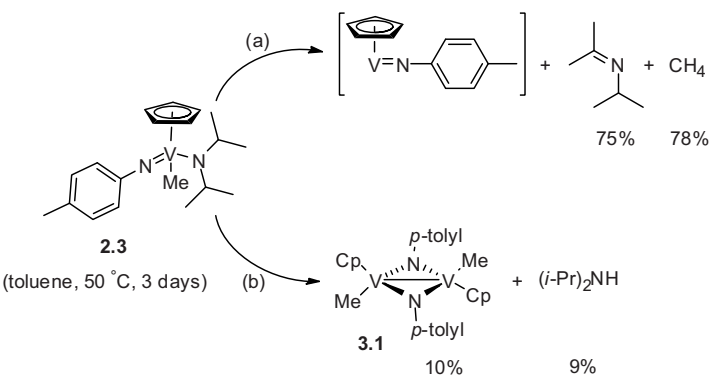


Scheme 2

In Chapter 2 the synthesis of cyclopentadienyl vanadium imido alkyl complexes with the diisopropylamido ligand were described. In this chapter the thermal stability of vanadium-methyl complexes (η^5-C_5H_5)(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) and (η^5-C_5H_5)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) is investigated. This provides a new route to CpV(III)-imido species.

3.2 Thermal stability of neutral vanadium(V) amido-imido complexes

Compound Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) is moderately stable at room temperature. Warming in toluene-d_8 at 50 °C over a period of 3 days leads to full conversion of the starting material, and the ^{1}H NMR spectrum indicates liberation of *N*-isopropyl-2-propanimine, diisopropylamine, methane, and generation of a mixture of diamagnetic [CpV(μ-N-*p*-tolyl)Me]$_2$ (**3.1**)[5] and an unidentified paramagnetic organovanadium species (Scheme 3). The amount of methane was measured by Toepler pump [0.78 CH_4 /V], and the amounts of *N*-isopropyl-2-propanimine and diisopropylamine were determined by integration using Cp_2Fe as an internal standard.



Scheme 3

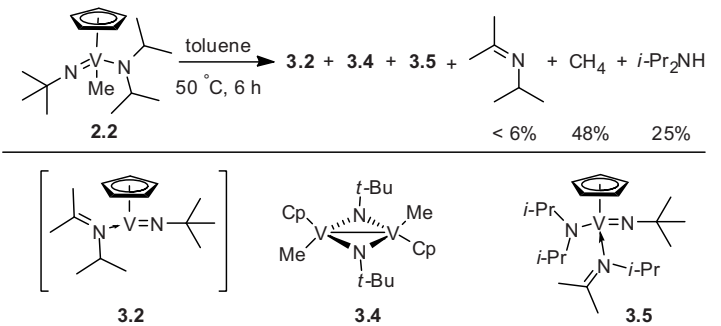
The organic products observed suggest that the thermolysis proceeds via two pathways: a major pathway (a) liberation of equimolar amounts of *N*-isopropyl-2-propanimine and methane, together with formation of a CpV(imido)-V(III) species, whose fate is as yet unclear; and a minor pathway (b) generation of a V(IV)-imido methyl species (which dimerizes), probably through release of a diisopropyl amine

radical,[7] which picks up a proton to form diisopropylamine. It is not clear where the amine hydrogen originates from.[8] The solvent can be excluded as hydrogen source as ^{2}H-NMR spectroscopy after thermolysis in toluene-d_8 did not show the presence of *i*-Pr_2ND. At the origin of the formation of the proposed CpV(imido)-V(III) species lies the relatively reactive methine proton of the diisopropylamido ligand, which is abstracted by the V-Me group to generate *N*-isopropyl-2-propanimine and methane in a 1:1 ratio. Thus, the major pathway in the thermolysis process would lead to formation of a CpV(imido)-V(III) species which, in the absence of Lewis bases, is expected to be paramagnetic and highly reactive. The diamagnetic imido-bridged dimer $[CpV(\mu\text{-N-}p\text{-tolyl})Me]_2$ (**3.1**) formed via pathway (b) (10% yield in the NMR-tube experiment but up to over 30% yield in an experiment on preparative scale) was synthesized previously by Buijink[5] from the reaction of the half-sandwich imido vanadium dichloride $CpV(N\text{-}p\text{-tolyl})Cl_2$ with $AlMe_3$.

The fate of the proposed "CpV(N-*p*-tolyl)" fragment is difficult to ascertain from this experiment. The presence of a paramagnetic species can be inferred from broad absorptions in the ^{1}H NMR spectrum (see Experimental section) but it is unclear whether this is a V(III) or V(IV) species. Therefore the reaction mixture was studied by EPR spectroscopy as V(IV) (S = 1/2) usually gives well-resolved spectra, whereas V(III) (S = 1) is EPR-'silent'.[9,10] Spectra were recorded at 77 K and at ambient temperature in toluene and benzene solvent. In all cases, no signal was observed, indicating that the paramagnetic species formed during thermolysis are EPR-silent and likely to be V(III).

Attempts at oxidizing "CpV(N-*p*-tolyl)" to the known $CpV(N\text{-}p\text{-tolyl})Cl_2$[1] or $[CpV(\mu\text{-N-}p\text{-tolyl})Cl]_2$[5] species by addition of the oxidant $PbCl_2$ to the reaction mixture after completion of the thermolysis did not yield recognizable products. Neither did addition of the diphosphine dmpe to the mixture at this time afford the CpV(N-*p*-tolyl)(dmpe) complex. As this compound is formed when dmpe is present *during* thermolysis (see section 3.2), it suggests that the "CpV(N-*p*-tolyl)" fragments generated in the thermolysis are highly reactive, and, in the absence of stabilizing agents, react further to give species that are as yet unidentified.

The *t*-Bu-imido compound **2.2** is more thermolabile than its *p*-tolyl-imido analogue **2.3**. It decomposes gradually at ambient temperature, and at 50 ºC decomposition is complete within 6 h. ^{1}H NMR spectroscopy shows the presence of diisopropylamine (25 %), and only a small amount of *N*-isopropyl-2-propanimine (< 6 %), plus liberation of methane (0.48 CH_4/V by Toepler pump) (Scheme 4).



Scheme 4

The formation of the organic products was confirmed by GC-MS analysis as well. As in the thermolysis of **2.3**, the diisopropylamine is not deuterated when the reaction is performed in deuterated solvent. Again, both diamagnetic and paramagnetic organometallic compounds are formed. For the paramagnetic product broad ^{1}H NMR absorptions are observed in C_6D_6 at δ 91.45 ppm, δ 38.30 ppm, δ 17.55 ppm, δ 15.40 ppm, δ 12.11 ppm, δ 10.06 ppm, δ 5.02 ppm, and δ - 6.44 ppm. The two diamagnetic species (5% and 20%, respectively) are represented by two cyclopentadienyl resonances at δ 6.30 ppm and δ 5.27 ppm which have an approximate ratio of 1:4. Taking the absorption at δ 6.30 ppm (for the Cp group) and an additional resonance at δ -0.33 ppm, corresponding to a V-CH_3 moiety, into consideration together with the appearance of diisopropyl amine during thermolysis and the fact that the analogous compound **2.3** forms the dimer **3.1** (*vide supra*), the acquired spectral data are assigned tentatively to a dimeric vanadium (IV) [CpV(μ-N*t*-Bu)Me]$_2$ (**3.4**) species (Scheme 4). Vroegop[11] showed that the related titanium dimer [CpTi(μ-*t*-Bu)Cl]$_2$ is initially generated as the *trans* species, and this kinetic product then gradually converts thermally to the *cis* species as the thermodynamic product. In the thermolysis mixture of **2.2**, the ratio between the two diamagnetic species observed does not change over time.

The thermolysis products of **2.2** cover a wider spectroscopic range in the ^{1}H NMR spectrum for the paramagnetic species compared to **2.3** and it is unclear whether the species present are V(III) or V(IV). Investigation of the thermolysis mixture by EPR shows, in contrast to the observations of the thermolysis of the *p*-tolylimido analogue **2.3**, a well-defined signal that can be attributed to a species with $S = 1/2$, probably a mononuclear V(IV) (d^1 species). A typical octet hyperfine structure (^{51}V, I = 7/2, 99.8% natural abundance) is present 95 % in benzene solution at 298 K (Figure 1) with g = 1.97 and a (^{51}V) ~18 G.

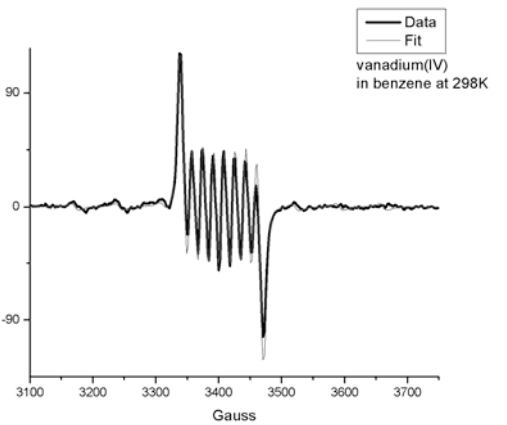
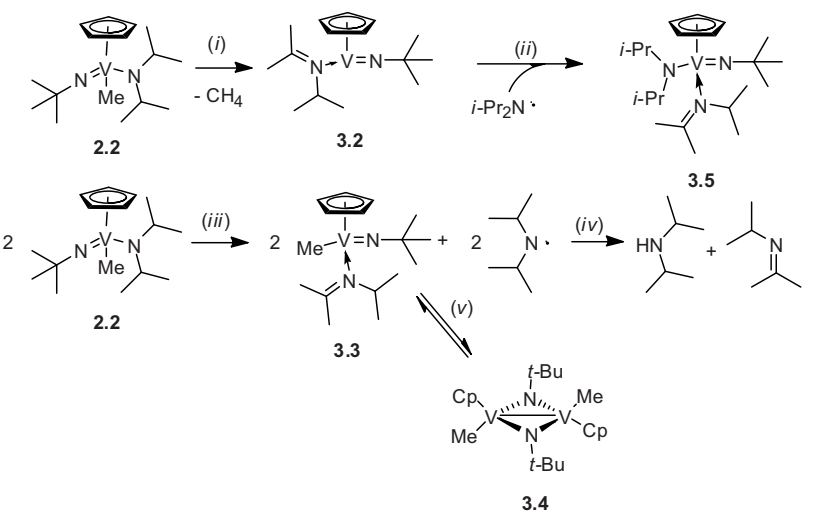


Figure 1. *EPR spectrum of the thermolysis mixture of compound **2.2** in benzene at 298K.*

Addition of $PbCl_2$ to the reaction mixture after the thermolysis and continued warming at 50 °C, revealed after 2 h the formation of one recognizable product: Cp(*i*-Pr_2N)V(N-*t*-Bu)Cl (**2.8**). Taking this into consideration together with the fact that the total amount of diisopropylamine and *N*-isopropyl-2-propanimine observed after thermolysis is only 31 %, suggests that the vanadium (IV) species recorded by EPR spectroscopy could be [Cp(*i*-Pr_2N)V(N-*t*-Bu)] (**3.5**) (Scheme 4). Moreover, addition of $PbCl_2$ reveals an increase of 20% of the *N*-isopropyl-2-propanimine suggesting that the ketimine is bound to a paramagnetic species in the thermolysis mixture. The ^{1}H NMR spectrum shows, after addition of $PbCl_2$, the formation of two main CpV-species in 1:2 ratio at δ 5.85 ppm of **2.8** and one at δ 5.83 ppm which could not be identified. Furthermore, no recognizable associated vanadium(V) organometallic product (*e.g.* CpV(N-*t*-Bu)Cl_2) could be observed,

possibly due to the fact that $PbCl_2$ is not sufficiently oxidizing to oxidize the V(III) to V(V). Although $PbCl_2$ has been used in vanadium chemistry to oxidize vanadium(II) complexes to vanadium(III), subsequent oxidation to vanadium(IV) did not occur.[12] This suggests the possibility that oxidation of V(III) species generated during thermolysis does not go further than V(IV) species. A small amount (<6 %) of the diamagnetic dinuclear V(IV) species $[CpV(\mu\text{-}Cl)N\textit{t}\text{-}Bu]_2$ [2e] could be observed.

Addition of dmpe to the mixture after thermolysis, in this case does generate a well-defined, diamagnetic species: the V(III) imido dmpe adduct Cp(*t*-BuN)V(dmpe) (**3.6**) (Scheme 6; the full synthesis and characterization of the compound is described in section 3.2). Additionally, ^{1}H NMR spectrum shows the presence of *N*-isopropyl-2-propanimine (ca. 22%) confirming the hypothesis of generating vanadium (III) species **3.2** (Scheme 4). Nevertheless, some paramagnetic species remain, as evidenced by the broad ^{1}H NMR resonances at δ 15.40 ppm, δ 12.11 ppm, δ 10.06 ppm and δ - 6.44 ppm, together with the diamagnetic species at δ 6.30 and δ 5.27 ppm. Based upon the spectral data and observed physical phenomena (*vide supra*) during the thermolysis of **2.2** an attempt was made to construct a mechanistic framework describing possible pathways leading toward the formation of **3.2**, **3.4** and **3.5** (Scheme 5).



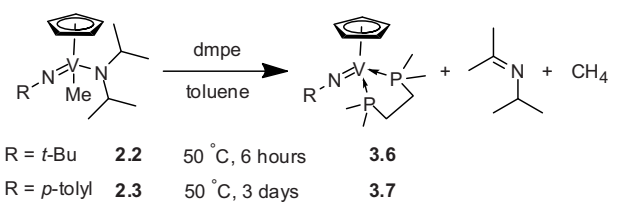
Scheme 5

Thermolysis of compound **2.2** follows similar pathways as proposed for its **2.3** analogue. The liberation of methane and *N*-isopropyl-2-propanimine from **2.2** leads toward the formation of transient species "CpV(N-*t*-Bu)" (**3.2**, *vide supra*) which can react further with a diisopropyl amine radical generating the vanadium (IV) species **3.5** (Scheme 5, pathways *i* and *ii*). Concurrently complex **2.2** undergoes homolytic V-N bond cleavage[7] (pathway *iii*) generating the isopropyl amine radical together with formation of CpV(IV)-imido methyl species **3.3** which most likely exists in equilibrium with its dimeric form **3.4** (pathway *v*). It is not clear where the hydrogen of the diisopropyl amine originates from, but disproportionation of amine radicals has been observed before (pathway *iv*).[8]

3.3 Trapping low-valent cyclopentadienyl vanadium (III) imido species

As discussed in the previous section, it appears that the major thermolysis pathway of the CpV(NR)(N*i*-Pr_2)Me (R = *p*-tolyl, *t*-Bu) species leads to a CpV(III)-imido moiety through liberation of *N*-isopropyl-2-propanimine and methane. As imido species of vanadium(III) are rare, we sought to trap these CpV(III) imido species selectively.

Thermolysis of **2.2** in an NMR tube in C_6D_6, in the presence of 1.2 equivalents of dmpe forms the adduct CpV(N-*t*-Bu)(dmpe) (**3.6**) selectively (Scheme 6). After 5 h at 50 °C, 94 % of the starting material **2.2** was converted to provide the dmpe-adduct **3.6** and the remaining 6% is unreacted starting material. The formation of the corresponding amounts of *N*-isopropyl-2-propanimine and methane (measured by Toepler pump 0.94 CH_4 /V) was observed.



Scheme 6

Thermolysis of the *p*-tolylimido compound **2.3** in the presence of dmpe in C_6D_6 showed (after 3 days at 50 °C) the formation of CpV(N-*p*-tolyl)(dmpe) (**3.7**) in 90 % conversion based on the internal standard (Scheme 6). In addition, formation of dimer [CpV(μ-N-*p*-tolyl)Me]$_2$ (**3.1**) (~ 6 %) was observed. Apparently, the addition of dmpe does not retard the radical decomposition pathway leading to the V(IV) dimer. The ^{1}H NMR spectrum confirms the presence of *N*-isopropyl-2-propanimine (88 % yield), diisopropyl amine (6 % yield), and methane. The amount of methane was measured by Toepler pump [0.84 CH_4 /V].

Both V(III) imido complexes were obtained on a preparative scale in 45-55% isolated yield after recrystallization as a crystalline material (green for **3.6**, purple for **3.7**), suitable for single-crystal X-ray diffraction. Their crystal structures are shown in Figure 2 with selected bond distances and angles in Table 1.

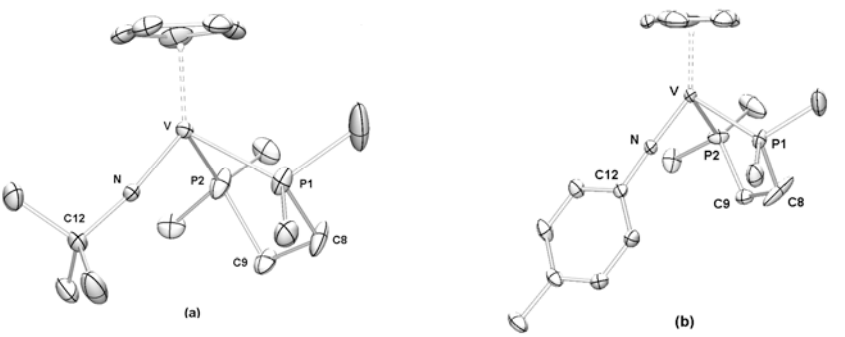


Figure 2. *Molecular structure of CpV(N-t-Bu)(dmpe), (**3.6**) – (a) and CpV(N-p-tolyl)(dmpe), (**3.7**) – (b) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.*

The molecular structures of **3.6** and **3.7** are quite similar; the compounds have a simple piano-stool geometry. The V-N distances (1.6903(1) Å and 1.7193(18) Å for **3.6** and **3.7** respectively) are characteristic for V-N multiple bond and are similar to those found in the literature[5] together with the nearly linear V-N-C(12) angles of 172.15(16)° (**3.6**) and 172.13(16)° (**3.7**) (CpVNC(*t*-Bu)=CH(*t*-Bu)(dmpe) 172.5(2)° [5]).

Table 1. *Selected bond lengths (Å) and angles (°) for* ***3.6*** *and* ***3.7****.*

Bond lengths (Å)	**3.6**	**3.7**
V – N	1.6903(1)	1.7193(18)
V – P1	2.3507(7)	2.3596(7)
V – P2	2.3522(7)	2.3522(7)
V – Cg*	2.277(9)	2.275(6)
N – C12	1.451(3)	1.380(3)
Bond angles (°)		
V – N – C12	172.15(16)	172.13(16)
P1 – V – P2	80.95(2)	80.95(2)
V – P2 – C9	104.81(17)	105.26(1)
V – P1 – C8	113.64(3)	109.56(10)
P1 – V – N	96.56(6)	94.42(6)
P2 – V – N	96.26(6)	88.41(6)
P1 – C8 – C9	107.36	113.04
P2 – C9 – C8	106.47	112.77

* Cg is the centroid of the C(1) - C(5) ring.

The coordination of the phosphorus to vanadium center in the new complexes formed is indicated by a typical 'horned' plateau (due to the ^{51}V nucleus) in the ^{31}P NMR spectrum (δ 87.34 ppm ($\Delta\nu_{top}$= 2696 Hz) for **3.6** and δ 87.41 pm ($\Delta\nu_{top}$= 2485 Hz) for **3.7** (Figure 3).

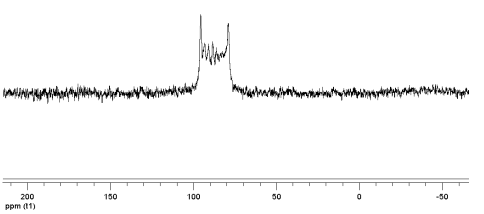


Figure 3. *^{31}P NMR spectrum of CpV(N-p-tolyl)(dmpe) (**3.7**).*

The ^{51}V NMR spectroscopic data for the imido-vanadium dmpe-adducts described in this chapter and for a number of relevant vanadium complexes are collected in Table 2. Comparing the ^{51}V NMR chemical shifts of V(N-*p*-tolyl)Cl_3 and V(N-*t*-Bu)Cl_3, the latter appear further downfield due to less electron donating ability of the *p*-tolyl imido ligand compared to the *t*-Bu imido ligand. Table 2 shows considerable chemical shift differences between the complexes upon replacement of the chlorine ligands, and upon changing from a chelating diphosphine to monodentate phosphines.

Table 2. *^{51}V NMR spectroscopic data for V(III)-imido-phosphorus adducts and related complexes in C_6D_6 at 25 °C.*

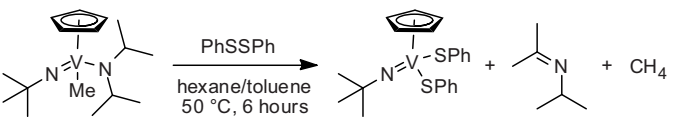
complex	*δ (^{51}V)*	*$\Delta\nu_{1/2}$ [Hz]*	*reference*
V(N-*p*-tolyl)Cl_3	305	500	[1]
CpV(N-*p*-tolyl)Cl_2	-240	790	[1]
V(N-*t*-Bu)Cl_3	8	315	[13]
CpV(N-*t*-Bu)Cl_2	-457	400	[2d]
Cp(*i*-Pr_2N)V(N*t*-Bu)Me (**2.2**)	-668 (t)	$J_{V\text{-}N}$ = 87 Hz	this work, [17]
Cp(*i*-Pr_2N)V(N*p*-tolyl)Me (**2.3**)	-600	320	this work, [17]
CpV(N-*p*-tolyl)(dmpe) (**3.7**)	-4.9 (t)	$J_{P\text{-}V}$= 341 Hz	this work
CpV(N-*t*-Bu)(dmpe) (**3.6**)	-381	5190	this work
CpV(N-*t*-Bu)(PMe_3)$_2$ (**3.8**)	-111 (t)	$J_{V\text{-}P}$ = 421 Hz	this work, [6b]
CpV(N-*t*-Bu)(PMe_3)(CO)	-746 (dt)	$J_{V\text{-}P}$ =406 HZ	[6a]
CpV(N-*p*-tolyl)(PMe_3)$_2$ (**3.9**)	268 (t)	$J_{V\text{-}P}$ = 399 Hz	this work

It is expected that a chelating diphosphine like dmpe strongly diminishes the reactivity of the V(III) imido species. Related compounds with two monodentate phosphines are expected to be significantly more reactive. In an NMR tube experiment in C_6D_6, **2.2** was warmed in the presence of PMe_3 (1:2 ratio) for 5 h at 50 °C. The ^{1}H and ^{31}P NMR spectra of the reaction mixture indicated full conversion of the starting material to CpV(N-*t*-Bu)(PMe_3)$_2$ (**3.8**), plus equimolar amounts of *N*-isopropyl-2-propanimine and methane. Compound **3.8** was

synthesized previously by Preuss and coworkers[6a] by reaction of CpV(N-*t*-Bu)Cl_2 with Mg in the presence of 2 equivalents of PMe_3 (72% yield). Both methods can generate **3.8** in good yields. Treatment of **2.3** with PMe_3 in 1:2 ratio (NMR tube experiment) in benzene-d_6 generated CpV(N-*p*-tolyl)$(PMe_3)_2$ (**3.9**) after 48 h at 50 ºC (82 % conversion based on the internal standard Cp_2Fe). ^{1}H NMR spectroscopy confirms the presence of the dimer **3.1** in ~ 5 % yield and the presence of broad resonances of paramagnetic species (the same species as observed when the thermolysis is performed without trapping agents). Moreover, the ^{31}P NMR spectrum shows the presence of both coordinated and non-coordinated phosphine in the mixture, indicating that PMe_3 is less efficient than chelating dmpe in trapping.

3.4 Trapping CpV(III) imido species with oxidizing reagents

As was shown in Section 3.1, the thermal decomposition of compounds **2.2** and **2.3** generates predominantly V(III) imido species. These should also be able to perform oxidative addition reactions. A well-known reagent for both 1e and 2e oxidation of low-valent transition-metal compounds is PhSSPh.[14] Warming a toluene/hexane solution of **2.2** with added PhSSPh to 50 ºC for 6 h provided an intensely green solution. Although the product could only be isolated as an oil, ^{1}H and ^{13}C NMR spectroscopy indicated the formation of the V(V) dithiolate CpV(=N*t*-Bu)$(SPh)_2$ [2h] (**3.10**) (Scheme 7), with two thiophenolate groups per CpV-fragment (based on ^{1}H NMR integration).

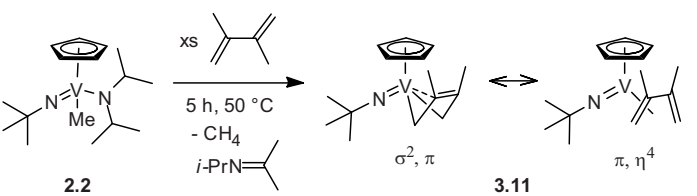


2.2 **3.10**

Scheme 7

Thus the V(III) species generated in the thermolysis of **2.2** can readily perform oxidative addition reactions. This is potentially useful for catalytic reactions (see section 3.4).

When 1,3-butadienes bind to low-valent transition-metal centers, π-back donation into the diene π_3* orbital can give the diene more or less σ^2,π-metallacyclopentene character (depending on the reducing ability of the metal fragment).[15,16,23] Analogous with the above experiment, 2,3-dimethyl-1,3-butadiene was used to trap the vanadium (III) imido intermediate in the thermolysis of **2.2**. NMR spectroscopy indicates that indeed the diene complex CpV(N-*t*-Bu)(C_6H_{10}) (**3.9**) is formed as the main product in the reaction (Scheme 8). Nevertheless, in the ^{1}H NMR spectrum of the material after evaporation of the volatiles (Figure 4) some impurities can be seen in the aliphatic region (1-2 ppm). Unfortunately, the products could be isolated only as an oil, despite numerous crystallization attempts, precluding structural analysis.



Scheme 8

The broadness of the ^{1}H and ^{13}C NMR absorptions of the diene V-CH_2 group (^{1}H: δ 3.85 ppm and δ -0.58 ppm for *syn* and *anti* protons; ^{13}C: δ 65.3 ppm) precludes the determination of the $^2J_{HH}$ and $^1J_{CH}$ coupling constants, which would normally provide information on the degree of diene reduction.

The ability of the butadiene ligands to stabilize early transition metals in low oxidation states lies in the resonance stabilization between the limiting σ^2,π (metalacyclopentene) and π,η^4(diene) structures. In the σ^2,π - character the diene has more the character of a butenediyl dianion, which corresponds to a formal oxidative addition of the diene to the metal center, in this case from V(III) to V(V). The V-butadiene complexes known so far exhibit mostly structures close to the π,η^4 binding mode (e.g. (η^5,η^1-$C_5H_4(CH_2)_2N$*i*-Pr)V(η^4-C_6H_{10}) (V(II)),[17] (η^5,η^1-$C_5H_4(CH_2)_2NMe_2$)V(η^4-C_6H_{10}) (V(I)),[16] (η^5-C_5H_5V(1,3-diene)PMe_3 (V(I)),[18,19]). To the best of our knowledge compound **3.11** appears to be the first example of a V(III) 1,3-butadiene complex.

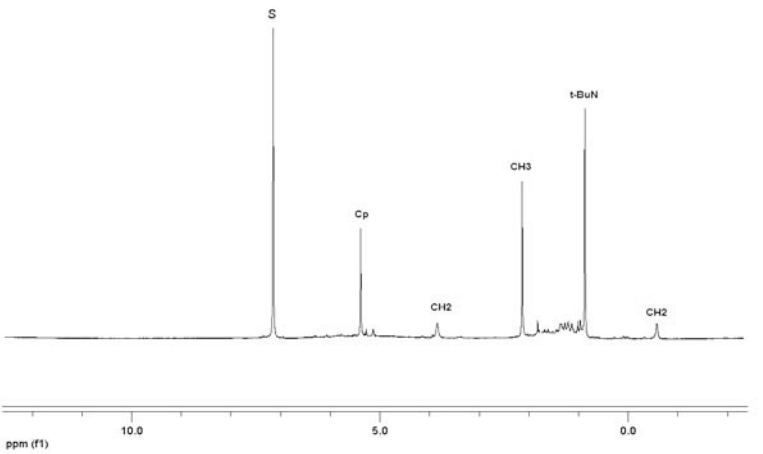


Figure 4. *^{1}H NMR spectrum of complex **3.11**.*

When the thermolysis of **2.3** was performed in the presence of 2,3-dimethyl-1,3-butadiene (50 °C for 72 h), the formation of CpV(N-*p*-tolyl)(C_6H_{10}) is observed, although the vanadium dimer [CpV(μ-N-*p*-tolyl)Me]$_2$ and the paramagnetic species as found when the thermolysis is performed without a trapping agent, are generated as well.

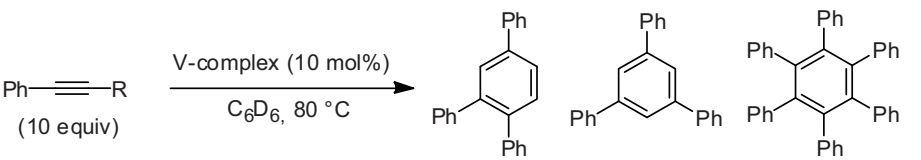
3.5 Further reactivity of the CpV(III)-imido species

Catalytic cyclotrimerization of alkynes. Several classes of low-valent transition-metal complexes are known to catalyze alkyne cyclotrimerization.[20,21] When the thermolysis of compounds **2.2** and **2.3** is performed in the presence of excess alkyne (phenylacetylene, diphenylacetylene) cyclotrimerization products (substituted benzenes) are formed catalytically. The low valent vanadium species generated in the thermolysis seems to be responsible for this catalysis.

In a NMR tube reaction, phenylacetylene addition to a solution of **2.2** or **2.3** in C_6D_6 (ratio 10:1 alkyne:vanadium) followed by warming to 80 ºC for 8 h and 28 h respectively, resulted in the formation of cyclotrimerization products (Table 3). The reactions were followed in time by ^{1}H NMR spectroscopy to full conversion of phenylacetylene. Gas chromatography (GC) and gas chromatography-mass

spectrometric (GC-MS) analyses confirmed formation of a mixture of the two isomers: 1,3,5- and 1,2,4- triphenylbenzene (1:1.2 ratio in 64 % yield for **2.2**; 1:1.5 ratio in 65 % for **2.3**). Although most of the phenylacetylene is consumed, the major products observed do not account for all of the material converted, hence other side reactions that consume phenylacetylene are occurring during this process. For **2.2** ca. 10 % of the remaining mixture was identified as tetramer (Mw = 420, n=4) and a single unidentified phenylacetylene dimer isomer as seen by GC-MS data (< 5 %). Oligomers (structurally undetermined tetramers and pentamers with Mw = 414 and Mw = 514 in GC-MS, ca. 10 %) and phenylacetylene dimer (ca. 12 %) are also present when neutral vanadium complex **2.3** is employed.
The cyclotrimerization product of diphenylacetylene (hexaphenylbenzene) was obtained in 71% isolated yield by warming a mixture of **2.3** with diphenylacetylene in C_6D_6 (ratio 20:1 alkyne:vanadium) for 60 h at 80 ºC (Table 3).

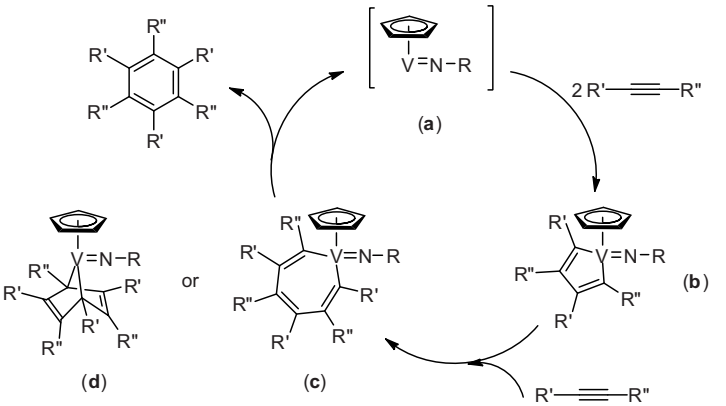
Table 3. The cyclotrimerization reaction of phenylacetylene and diphenylacetylene with neutral vanadium systems **2.2** and **2.3**.



entry	V-complex	R	time (h)	alkyne # conv(%)	yield (%)	product ratio
1	**2.2**	H	8	88	64[a]	**a**:**b** = 1.2:1
2	**2.3**	H	28	90	65[a]	**a**:**b** = 1.5:1
3	**2.3**	Ph	60	80	71[b]	**c**

[#] Determined by ^{1}H NMR; [a] yield determined by GC analysis; [b] isolated yield.

A proposed mechanism for this process[21] is presented in Scheme 9, which involves initial oxidative coupling of two alkynes on the V(III) imido species (**a**) to give a metallacyclopentadiene (**b**).



Scheme 9

Two modes of reaction of alkynes with metallacyclopentadiene have been suggested: (*i*) insertion of a third alkyne molecule into one of the V-C bonds to give a complex such as **c**[21c] and (*ii*) a Diels-Alder addition of a coordinated alkyne to the diene moiety of the metallacyclopentadiene (**b**) generating the bicyclic intermediate **d**[22]. Reductive elimination then releases the formed arene product and regenerates the V(III) species.

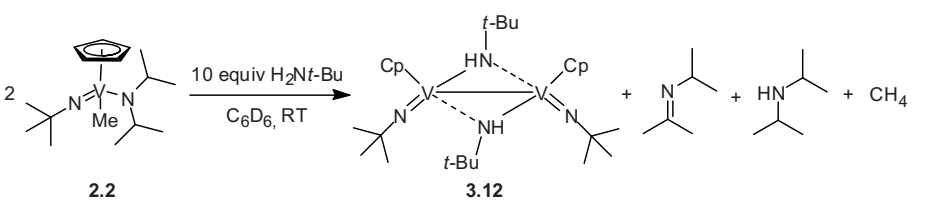
In Section 3.2 it was shown that CpV(III)-imido species could be trapped with phosphines. It is expected that these will retard or even quench the catalytic activity towards unsaturated substrates. To investigate this, compounds **3.6**, **3.7** and **3.8** were treated with an excess of phenylacetylene (molar ratio = 1:10). The reactions were followed by NMR spectroscopy and the products were analyzed by GC-MS analysis. With compound **3.8,** 35 % conversion of the phenylacetylene was observed after 2 h at 80 ºC, and after 4 h the conversion reached 65 % (based on integration of the ^{1}H NMR spectrum versus Cp_2Fe as an internal standard). 10 minutes after the addition of alkyne, the ^{31}P NMR spectrum indicated the presence of non-coordinated PMe_3, whereas after 4 h most of the PMe_3 has been liberated. GC and GC-MS analyses of the crude mixture confirmed the formation of a 1:3 ratio of 1,3,5- and 1,2,4-triphenylbenzene with a total yield of 45 %. Apart from the substituted benzenes, ca. 8 % dimer and 10 % tetramer (Mw = 420, n=4) were formed as well. In the absence of phosphorus donors, the CpV(III)-imido species converted the phenylacetylene completely within 4 h generating 65 %

cyclotrimerization products (although other side products are present as well), whereas with the bis(trimethylphosphine) adduct **3.8** a 45 % conversion of the phenylacetylene into substituted benzenes products was achieved.

Preuss and coworkers[6a] have reported that treatment of CpV(N-*t*-Bu)(PMe_3)$_2$ with alkyne (2-butyne, diphenylacetylene) (molar ratio = 1:1) resulted, after 24 h at room temperature, in the formation of CpV(N-*t*-Bu)(PMe_3)(η^2-RCCR) (R = Me, Et, Ph) and CpV(N-*t*-Bu)(PMe_3)(η^2-HCCR) (R = Ph, $SiMe_3$, OEt) complexes. One of the PMe_3 group was replaced, although catalytic activity was not investigated further with these compounds.

The dmpe adducts **3.6** and **3.7** show catalytic activity towards phenylacetylene as well, although slower compared to **3.8**. The ^{1}H NMR spectrum indicates 60 % conversion of the phenylacetylene within 20 h at 80 ºC (for **3.7**) (based on internal standard Cp_2Fe) and full conversion after 72 h at 80 ºC; ^{31}P NMR indicates that after this time most of the dmpe has been liberated. The GC-MS/GC analyses confirms the formation of the two cyclotrimerization isomers 1,2,4- and 1,3,5-triphenylbenzene (Mw = 306) in a ratio 1.4:1 for **3.7** and a ratio of 1:0.8 for **3.6**. In both cases the formation of phenylacetylene dimer is observed as well (ca. 7 %/**3.6** and 15 %/**3.7**). Thus, the presence of phosphines ligands diminishes the catalytic activity of the CpV(III)-imido species, but does not suppress it completely even with the bi-dentate dmpe.

Reaction with tert-butyl amine. Treatment of **2.2** with an excess of *t*-BuNH_2 in benzene results in the formation of the stable 18 v.e. vanadium(IV) dimer [CpV(N-*t*-Bu)(μ-NH*t*-Bu)]$_2$ (**3.12**) (Scheme 10).



2.2 **3.12**

Scheme 10

In an NMR-tube experiment in C_6D_6, **3.12** begins to precipitate from the solution in about 10 minutes after the amine addition. ^{1}H NMR spectroscopic analysis reveals

the presence of both diisopropyl amine and *N*-isopropyl-2-propanimine in a ratio of 1:2 respectively, together with the new species formed and methane. Moreover, not all of the starting material was converted immediately into the compound **3.12**. Full conversion of the starting material was achieved upon prolonged reaction time (ambient temperature, 5 days), after which the ratio diisopropyl amine to *N*-isopropyl-2-propanimine did not change. If, after 2 h at RT from amine addition when the ketimine : diisopropyl amine ratio is 2:1, the NMR-tube is placed at 50 ºC for 24 h, the amount of *N*-isopropyl-2-propanimine becomes 4 times higher than the diisopropyl amine formed. The observed difference in amine : imine ratio for the low and high temperature pathways suggests that they may proceed via different mechanisms. The low temperature pathway most probably involves protonation of either the V-Me, V-N*i*-Pr_2 or V=N-*t*-Bu bond leading toward formation of dimer **3.12**. It is difficult to predict though which bond is most likely to be protonated. The high temperature pathway starts with usual *N*-isopropyl-2-propanimine and methane elimination which followed by an oxidative addition of amine together with expulsion of H_2 would lead to formation of the observed product. However, the exact pathway could not be deduced based on the acquired data.

On a preparative scale, [CpV(N-*t*-Bu)(μ-NH-*t*-Bu)]$_2$ (**3.12**) was isolated as a red-brown crystals from pentane (65 % yield), after stirring overnight at room temperature. The molecular structure of **3.12** is depicted in Figure 5 (Table 4 contains selected bond distances and angles).

The HN proton resonance of [CpV(=N-*t*-Bu)(μ-NH-*t*-Bu)]$_2$ (**3.12**) appears in the solution ^{1}H NMR spectrum at δ 1.79 ppm and the *t*-Bu groups show two inequivalent signals (δ 1.37 ppm and 1.27 ppm). In the solid state, the two cyclopentadienyl moieties adopt a *syn* geometry relative to the central V_2N_2 core. The two hydrogen atoms of the bridged μ-NH-*t*-Bu are virtually perpendicular to the V_1-N_2-V_2-N_3 plane). From Table 4, it follows that the angle sum of V_1-N_2-V_2-N_3 is 359.97°, indicating the planarity of the central four-membered ring. The V1-V2 distance of 2.876 Å lies in the range associated with a metal-metal bond between V(IV) centers.[23,24,25]

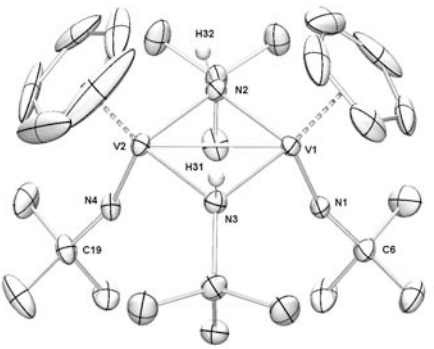


Figure 5. *Molecular structure of [CpV(=N-t-Bu)(μ-NH-t-Bu)]$_2$ (***3.12***) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity, except for the μ-NHt-Bu.*

Table 4. *Selected bond lengths (Å) and angles (°) for [CpV(N-t-Bu)(μ-NH-t-Bu)]$_2$ (**3.12**).*

Bond lengths	(Å)	Bond angles	(°)
V1 – N1	1.677(4)	V1 – N1 – C6	161.2(3)
V1 – N2	2.072(4)	V2 – N4 – C19	161.8(3)
V1 – N3	2.085(5)	N2 – V2 – N3	92.82(17)
V1 – Cg*	1.692	N2 – V1 – N3	92.81(17)
V2 – N2	2.077(4)	V1 – N2 – V2	87.34(17)
V2 – N3	2.079(5)	V1 – N3 – V2	87.97(17)
V2 – N4	1.676(4)	N2 – V1 – N1	105.60(19)
V2 – Cg*	1.686	N1 – V1 – N3	105.99(18)
V1 – V2	2.876	N3 – V2 – N4	106.26(8)
		N2 – V2 – N3	105.46(8)

* Cg is the centroid of the C(1) - C(5) ring.

Although the metal in compound **3.12** is a d^1 center, in solution it displays diamagnetic behavior due to the coupling of the unpaired electrons of the vanadium centers, most probably through the V-V bond. Preuss and coworkers[25] reported a related dinuclear V(IV) imido-alkoxide compound (isolated from attempted alkylation of Cp(*t*-BuN)VCl(O-*t*-Bu) with Li-alkyl reagents), to which they

assigned the structure [CpV(μ-N-*t*-Bu)(O-*t*-Bu)]$_2$ (**3.13**), with bridging *t*-Bu-imido ligands. Both structures **3.12** and **3.13** have the cyclopentadienyl rings in a *syn* position. The V2-N1-V1 angle in **3.13** of 97.6(1)° is much larger than the one in **3.12** (87.97(17)° and 87.34(17)°). A remarkable feature is that the reported V1-O1 and V2-O2 distances in **3.13** (1.676(6)Å and 1.650(5)Å) are much too short compared to that expected for a normal V-O bond (1.88 Å, based on Pauling radii[26]). The observed distances correspond more to a V=N bond as in compound **3.12** (Table 2, V1=N1 of 1.677(4)Å and V2=N4 of 1.676(4)Å). It therefore could be that the correct formulation of Preuss' compound **3.13** is in fact [CpV(N-*t*-Bu)(μ-O-*t*-Bu)]$_2$ with terminal imido groups and the monoanionic ligands bridging the metals, as is the case in **3.12**.

Once formed, the dinuclear complex **3.12** cannot be broken up into monomeric units by Lewis bases such as THF or pyridine. Pyridine was added to **2.2** before the addition of *t*-BuNH$_2$, but even with a large excess of pyridine present the formation of the dimer could not be prevented.

3.6 Concluding remarks

Electronically unsaturated CpV(III)-imido compounds form a class of highly reactive species that are readily available (in the absence of external reducing agents) from Cp(*i*-Pr_2N)V(N-R)Me. The trivalent metal center is generated in a thermolysis process involving β-H transfer from the V-N*i*-Pr_2 group, as suggested by the formation of the organic co-products *N*-isopropyl-2-propanimine and methane. Nevertheless, an additional (minor) pathway is present that appears to involve V-N homolysis, leading to V(IV).

It appears that under the thermolysis conditions, changing the imido substituent from a less electron-donating (*p*-tolyl, **2.3**) to a more electron-donating group (*t*-Bu, **2.2**) influences the reactivity of the vanadium center, giving a different product from the homolysis reaction. Whereas for the thermal decomposition of **2.3** this leads to a diamagnetic dinuclear V(IV) species, the thermolysis of **2.2** generates also a monomeric vanadium (IV) species as shown by EPR spectroscopic analysis. Performing the thermolysis process in the presence of phosphines can effectively trap the CpV(III)-imido moieties selectively. These CpV(III)-imido species can undergo oxidative addition, and show catalytic activity towards alkynes, generating cyclotrimerization products, in the presence or absence of phosphines. Nevertheless, the activity is diminished by the presence of PMe_3 and to a larger extent by the presence of the chelating diphosphine dmpe. The highly reactive 'CpV=N-*t*-Bu' species can also be trapped by 2,3-dimethyl-1,3-butadiene, generating the first V(III) 1,3-butadiene complex.

3.7 Experimental section

For general considerations see Chapter 2 (page 37). In addition: compound PMe_3[27] was synthesized according to a literature procedure. 2,3-Dimethyl-1,3-butadiene was dried over $MgSO_4$, filtered and distilled before use. The *t*-$BuNH_2$ and PhCCH were dried over CaH_2 and distilled prior use. Diphenylacetylene was sublimed before use, and compounds PhSSPh, 1,2-bis(dimethylphosphino)ethane (dmpe) were used as purchased. EPR spectra (X-band, 9.46 GHz) were recorded on a Bruker ECS106 instrument. GC analyses were performed on a HP 6890 instrument with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. The syntheses of the compounds **2.2** and **2.3** were reported in Chapter 2.

Thermolysis of Cp(*i*-Pr_2N)VMe(N-*t*-Bu) (2.2)

In an NMR tube equipped with a Teflon (Young) valve, a solution was made of **2.2** (0.050 g, 0.17 mmol) in C_6D_6 (0.6 mL). The tube was attached to the vacuum line and evacuated three times after which the tube was placed in the oven at 50 ºC for 6 h. After the decomposition was complete the tube was attached again to the vacuum line and the amount of methane formed in the reaction was determined using a Toepler pump (0.48 CH_4/V). Afterwards, the volatiles were transferred to a second tube and analyzed by ^{1}H NMR (Cp_2Fe was used as internal standard) and GC-MS. These confirmed the presence of diisopropylamine (m/z = 101) and *N*-isopropyl-2-propanimine (m/z = 99) in 25 % and 6 % yield respectively. To the residue, fresh C_6D_6 was added. ^{1}H NMR analysis revealed the presence of both diamagnetic and paramagnetic species. The latter exhibits broad resonances ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 91.45 (br, $\Delta\nu_{1/2}$ = 336 Hz), 58.88 (br, $\Delta\nu_{1/2}$ = 257 Hz), 38.30 (br, $\Delta\nu_{1/2}$ = 96 Hz), 17.55 (br, $\Delta\nu_{1/2}$ = 234 Hz), 15.40 (br, $\Delta\nu_{1/2}$ = 390 Hz), 12.07 (br, $\Delta\nu_{1/2}$ = 156 Hz), 10.06 (br, $\Delta\nu_{1/2}$ = 208 Hz), 5.02 (br, $\Delta\nu_{1/2}$ = 345 Hz), - 6.44 (br, $\Delta\nu_{1/2}$ = 1375 Hz). The diamagnetic species are represented in the cyclopentadienyl area by two major resonances at δ 6.30 ppm and δ 5.27 ppm in 1:2 ratio.

NMR data for *i*-Pr_2NH and $(CH_3)_2C=N(i\text{-}Pr)$.

^1H NMR (400 MHz, C_6D_6, 25 °C) for *i*-Pr_2NH: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 2.79 (sept, J_{HH} = 6.2 Hz, 2H CH *i*-Pr_2N), 0.96 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), 0.23 (s broad, 1H NH). (400 MHz, C_6D_5Br, 25 °C): δ 2.80 (sept, J_{HH} = 6.2 Hz, 2H CH *i*-Pr_2N), 0.95 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), 0.44 (s broad, 1H NH).

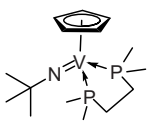
^1H NMR (400 MHz, C_6D_6, 25 °C) for $(CH_3)_2C=N(i\text{-}Pr)$: 3.44 (sept, J_{HH} = 6.2 Hz, 1H CH *i*-Pr_2N), 1.80 (s, 3H CH_3), 1.36 (s, 3H CH_3), 1.15 (d, J_{HH} = 6.2 Hz, 6H, CH_3 *i*-Pr_2N).

Thermolysis of Cp(*i*-Pr_2N)VMe(N-*p*-tolyl) (2.3)

A solution of **2.3** (0.40 g, 1.2 mmol) in toluene (3 mL) was warmed at 50 °C over a period of 3 days after which the decomposition was complete. Slow cooling to room temperature afforded red-brown crystals, which were separated from the rest of the mixture. The ^1H NMR spectrum of the crystals indicates the formation of the diamagnetic complex $[CpV(\mu\text{-}N\text{-}p\text{-tolyl})Me]_2$ (**3.1**),[5] obtained in 30 % isolated yield. From the remaining mixture, the toluene was removed in *vacuo* and the crude residue was stripped with pentane (2 x 1 mL), resulting a green oil. ^1H NMR analysis of the oil reveals the presence of paramagnetic species. ^1H NMR (400 MHz, C_6D_6, 25°C): δ 39.72 (br, $\Delta\nu_{1/2}$ = 403 Hz), 28.55 (br, $\Delta\nu_{1/2}$ = 340 Hz), 19.02 (br, $\Delta\nu_{1/2}$ = 276 Hz), 16.29 (br, $\Delta\nu_{1/2}$ = 177 Hz), 9.32 (br, $\Delta\nu_{1/2}$ = 193 Hz), 5.38 (br, $\Delta\nu_{1/2}$ = 33 Hz), -5.21 (br, $\Delta\nu_{1/2}$ = 25 Hz), -8.44 (br, $\Delta\nu_{1/2}$ = 52 Hz).

NMR tube experiment: In an NMR tube equipped with a Teflon (Young) valve, a solution was made of **2.3** (0.055 g, 0.16 mmol) in benzene-d_6 (0.6 mL). The tube was attached to the vacuum line and evacuated three times after which the tube was placed in the oven at 50 ºC for 3 days. After the decomposition was complete the tube was attached again to the vacuum line and the amount of methane formed in the reaction was determined using a Toepler pump (0.78 CH_4 /V). Afterwards, the volatiles were transferred to a second tube which contains Cp_2Fe and analyzed by ^1H NMR and GC-MS. The analyses confirmed the presence of *N*-isopropyl-2-propanimine (m/z = 101) and diisopropylamine (m/z = 99) in 75 % and 9 % yield respectively.

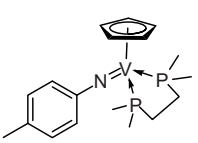
Synthesis of CpV(N-*t*-Bu)(dmpe) (3.6)



Dmpe (0.116 g, 0.771 mmol) was added at ambient temperature to a solution of (*i*-Pr_2N)CpVMe(N-*t*-Bu) (**2.2**) (0.233 g, 0.771 mmol) in toluene (20 mL). The red-brown solution was warmed to 50 ºC and stirred overnight. The solvent was removed *in vacuo* and the reaction mixture was stripped twice with pentane (5 mL). The residue was extracted with 20 mL of pentane. The solution was concentrated to 10 mL and cooled to – 80 ºC affording 0.10 g (0.30 mmol, 45 %) of green block shaped crystals of **3.5** suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 4.87 (s, 5H Cp), 1.41 ~ 1.28 (m, 6H P*Me*$_2$ overlap with 2H PC*H*$_2$), 1.27 (s, 9H, *t*-BuN), 1.10 (m, 2H PC*H*$_2$), 0.68 (m, 6H P*Me*$_2$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 89.88 (*C*H Cp), 34.60 (*C*H$_3$ *t*-BuN), 32.44 (P*C*H$_2$), 24.55 (P*Me*$_2$), 17.92 (P*Me*$_2$), C_q of *t*-Bu not observed. ^{31}P{^{1}H} NMR (100 MHz, C_6D_6 , 25°C): δ 87.34 (plateau, $\Delta\nu_{top}$= 2689). ^{51}V NMR (131 MHz, C_6D_6, 25 °C, $VOCl_3$ external standard): δ -381 ($\Delta\nu_{1/2}$ = 5190). Anal. Calcd.(%) for $C_{15}H_{30}NP_2V$: C, 54.54; H, 9.44; N, 3.98. Found: C, 54.1; H, 9.12; N, 4.21.

NMR tube experiment: In an NMR tube equipped with a Teflon (Young) valve, a solution was made of **2.2** (0.060 g, 0.20 mmol) in benzene-d_6 (0.6 mL) with equivalent of dmpe (0.030g, 0.20 mmol) added. The tube was attached to the vacuum line and evacuated three times after which the tube was placed in the oven at 50 ºC for 6 h. Subsequently the tube was attached again to the vacuum line and the amount of methane formed during the reaction was measured using a Toepler pump (0.94 CH_4 /V). ^{1}H NMR analysis confirmed the presence of *N*-isopropyl-2-propanimine.

Synthesis of CpV(N-*p*-tolyl)(dmpe) (3.7)

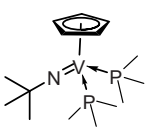


One equivalent of dmpe (0.12 g, 0.80 mmol) was added to a solution of Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) (0.27 g, 0.80 mmol) in toluene (20 mL). The reaction mixture was warmed to 50 ºC and stirred for 48 h. The solvent was removed in *vacuo* and the mixture was stripped twice with pentane (5 mL). The residue was extracted with 20 mL of pentane. Upon concentration the solution to 10 mL and cooling to – 80 ºC

0.164 g (0.44 mmol, 55%) of reddish purple blocks crystals of **3.6** were obtained, suitable for X-ray analysis. ^{1}H NMR (400 MHz, C_6D_6, 25°C): δ 7.06 (d, J_{HH} = 8.0 Hz, 2H *p*-tolylN), 6.90 (d, J_{HH} = 8.0 Hz, 2H *p*-tolylN), 4.99 (br, 5H Cp), 2.13 (s, 3H, CH_3 *p*-tolylN), 1.71-1.49 (m, 2H PC*H*$_2$), 1.43-1.32 (m, 6H, P*Me*$_2$), 1.17-0.97 (m, 2H, PC*H*$_2$), 0.67-0.45 (m, 6H, P*Me*$_2$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25°C): δ 128.96 (*C*H *p*-tolylN), 125.34 (*C*H *p*-tolylN), 92.58 (*C*H Cp), 32.16 (P*C*H$_2$), 21.15 (*C*H$_3$ *p*-tolylN), 17.51 (P*Me*$_2$). C_q of *p*-tolylN not observed. ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25°C): δ 87.51 (plateau, $\Delta\nu_{top}$=2449). ^{51}V NMR (131 MHz, C_6D_6, 25°C, $VOCl_3$ external standard): δ -4.90 (t, $J_{P\text{-}V}$= 340.9 Hz). Anal. Calcd.(%) for $C_{18}H_{28}NP_2V$: C, 59.07; H, 8.09; N, 3.63. Found: C, 58.7; H, 7.69; N, 3.82.

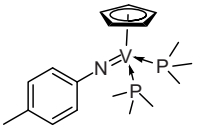
NMR tube experiment: In an NMR tube equipped with a Teflon (Young) valve, a solution was made of **2.3** (0.058 g, 0.172 mmol), dmpe (0.026 g, 0.172 mmol) and Cp_2Fe (0.032, 0.172 mmol, internal standard) in benzene-d_6 (0.6 mL). The tube was attached to the vacuum line and evacuated three times after which the tube was placed in the oven at 50 ºC for 3 days. Subsequently the tube was attached again to the vacuum line and the amount of methane formed during the reaction was measured using a Toepler pump (0.84 CH_4 /V). ^{1}H NMR analysis confirmed the presence of *N*-isopropyl-2-propanimine and diisopropyl amine in 88 % and 6 % respectively.

Generation of CpV(N-*t*-Bu)(PMe$_3$)$_2$ (3.8)



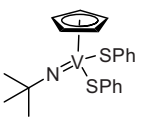
In an NMR tube equipped with a Teflon (Young) valve, a solution was made of Cp(*i*-Pr$_2$N)VMe(*t*-BuN) (**2.2**) (0.040 g, 0.13 mmol) in C_6D_6, to which PMe_3 (0.020 g, 0.26 mmol) was added. The tube was warmed at 50 °C for 6 h and the color changed to green-brown. The volatiles were removed *in vacuo*, affording compound **3.7** as a brown-green oil (86 % yield, Cp_2Fe internal standard) ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 4.81 (broad s, 5H Cp), 1.07 (s, 9H CH_3 *t*-BuN), 0.82 (broad s, 18H PMe_3). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 92.00 (*C*H Cp), 67.8 (*C*$_q$ *t*-BuN), 34.54 (*C*H$_3$ *t*-BuN), 25.02 (dd, J_{CP} = 9.6, 4.8 Hz, PMe_3). ^{31}P{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 52.30 (plateau, $\Delta\nu_{top}$= 2914.98). ^{51}V NMR (131 MHz, C_6D_6, 25 °C, $VOCl_3$ external standard): δ - 111.39 (t, $J_{V\text{-}P}$ = 420.58 Hz).

Generation of CpV(N-*p*-tolyl)(PMe_3)$_2$ (3.9)



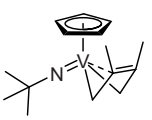
In an NMR tube equipped with a Teflon (Young) valve, a solution was made of **2.3** (0.03 g, 0.08 mmol) and Cp_2Fe (0.015 g, 0.08 mmol) in C_6D_6 (0.5 mL) to which PMe_3 (0.01 g, 0.02mL, 0.16 mmol) was added. This was kept at 50 °C for 48 h. After this time the color of the mixture had changed from red-brown to brown-green. The spectroscopic data confirmed the formation of **3.11** in 82 % yield (relative to Cp_2Fe internal standard). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.14 (d, J_{HH} = 8.1 Hz, 2H *p*-tolylN), 6.94 (d, J_{HH} = 7.7 Hz, 2H *p*-tolylN), 4.88 (broad s, 5H Cp), 2.16 (s, 3H CH_3 *p*-tolylN), 1.03 (m, 18H PMe_3). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25°C): δ 161.52 (*ipso-C p*-tolyl), 129.06 (*C*H *p*-tolylN), 128.72 (*ipso-C p*-tolyl), 125.56 (*C*H *p*-tolylN), 94.49 (*C*H Cp), 23.29 (dd, J_{CP} = 10.3, 5.9 Hz, PMe_3), 21.22 (*C*H_3 *p*-tolylN). ^{31}P{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 54.45 (plateau). ^{51}V NMR (131 MHz, C_6D_6, 25 °C, $VOCl_3$ external standard): δ 267.59 (t, $J_{V\text{-}P}$ = 399.66 Hz).

Synthesis of CpV(N-*t*-Bu)(SPh)$_2$ (3.10)



To a reddish brown solution of Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) (0.126 g, 0.420 mmol) in hexane (1 mL), a 1 mL hexane solution of PhSSPh (0.091 g, 0.42 mmol) was added. After 5 h at 50 °C the mixture turned deep green. The solvent was subsequently pumped off, leaving compound **3.8** as green oil. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.93 (d, J_{HH} = 7.7 Hz, 4H S-Ph), 7.12 (d, J_{HH} = 7.6 Hz, 4H S-Ph), 6.98-6.80 (m, 2H S-Ph), 5.61 (s, 5H CH Cp), 1.02 (s, 9H CH CH_3 *t*-BuN). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 148.81 (*ipso*-C S-Ph), 132.81 (*C*H S-Ph), 128.28 (*C*H S-Ph), 125.94 (*C*H S-Ph), 108.17 (*C*H Cp), 30.07 (*C*H_3 *t*-BuN), C_q of *t*-BuN not observed.

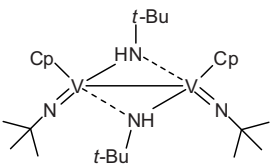
Synthesis of CpV(N-*t*-Bu)(C_6H_{10}) (3.11)



2,3-Dimethyl-1,3-butadiene (0.326 g, 3.97 mmol) was added to a reddish brown solution of Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) (0.200 g, 0.66 mmo) in pentane (1 mL). The reddish brown solution turned brown upon stirring at 50 °C for 5 h. The solvent was removed *in vacuo* and the residue was stirred once with pentane which was subsequently

removed *in vacuo*, affording compound **3.9** as brown oil (48 % yield, Cp_2Fe internal standard). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 5.39 (s, 5H Cp), 3.85 (broad s, 2H V-C*H*$_2$), 2.14 (s, 6H CMe), 0.87 (s, 9H CH_3 *t*-BuN), - 0.58 (broad s, 2H V-C*H*$_2$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 89.57 (*C*H Cp), 65.28 (V-*C*H$_2$, broad $\Delta\upsilon_{1/2}$ = 136.4 Hz), 53.62 (*ipso*-*C*, *t*-BuN), 31.46 (*C*H$_3$ *t*-BuN), 24.65 (*C*H$_3$ CMe). ^{51}V NMR (131 MHz, C_6D_6, 25 °C, $VOCl_3$ external standard): δ 616.24 (t, $J_{V\text{-}N}$ = 82.3 Hz).

Synthesis of [CpV(μ-NH-*t*-Bu)(N-*t*-Bu)]$_2$ (3.12)



To a solution of Cp(*i*-Pr$_2$N)VMe(N-*t*-Bu) (**2.2**) (0.2 g, 0.7 mmol) in 15 mL pentane, *t*-BuNH$_2$ (0.48 g, 6.7 mmol) was slowly added at room temperature. The mixture was stirred overnight. After all volatiles were removed *in vacuo* the resulting brown solid was stripped with 2 portions of 5 mL of pentane. Extraction with 15 mL of pentane, concentration of the solution and cooling at -80 °C yielded 0.22 g (0.43 mmol, 65 %) of brown, block shaped crystals of compound **3.1,** that were suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6, 25°C): δ 5.27 (s, 10H, Cp), 1.79 (s broad, 2H NH), 1.37 (s, 18H *t*-BuN), 1.27 (s, 18H *t*-BuN). ^{13}C NMR (100 MHz, C_6D_6, 25°C): δ 100.83 (CH Cp), 50.67 (*ipso*-C *t*-BuN), 45.28 (*ipso*-C *t*-BuNH), 23.94 (*C*H$_3$ *t*-BuN), 23.74 (*C*H$_3$ *t*-Bu). Anal. Calcd.(%) for $C_{26}H_{46}N_4V_2$: C, 60.69; H, 8.98; N, 10.85. Found: C, 60.18; H, 9.02; N, 10.78.

Catalytic cyclotrimerization of phenylacetylene using 2.2 and 2.3.

All cyclotrimerization experiments were performed in NMR tubes equipped with a Teflon (Young) valve. To a solution of **2.2** or **2.3** (0.045 mmol) in C_6D_6 (0.6 mL), 1 equivalent of cyclohexane (0.045 mmol, 5 μl added via micro-syringe) was added, followed by 10 equivalents of PhCCH (0.046 g, 0.45 mmol). The tube was placed at 80 ºC and monitored by ^{1}H NMR spectroscopy. After completion of the reactions, the mixtures were analyzed by GC-MS and GC as well, using the cyclohexane as internal standard (R_F = 1.02).

Catalytic cyclotrimerization of phenylacetylene using 3.5, 3.6 and 3.7.

The cyclotrimerization experiments were performed in NMR tubes equipped with a Teflon (Young) valve. To an NMR tube containing freshly generated **3.7** (0.10 mmol, 0.029 g) and Cp_2Fe (0.10 mmol, 0.018 g) in C_6D_6, PhCCH (0.96 mmol, 0.098 g) was added via a syringe. The tube was warmed at 80 °C and the conversion of the phenylacetylene was followed by NMR spectroscopy. After completion of the reaction, CH_2Cl_2 (0.1 mL) was added to the mixture, which was then analyzed by GC/MS. This showed the formation of 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene. The same procedure was employed when using **3.5** and **3.6**, with the exception that isolated material of these compounds were weighed in.

1,3,5-Triphenylbenzene/1,2,4-Triphenylbenzene[28,29]

^{1}H NMR (400 MHz, C_6D_6, 25 °C): 1,3,5-isomer, δ 7.85 (s, 3 H), 7.71-7.23 (m, 15 H); 1,2,4-isomer, δ 7.23-7.71 (m, 18 H). GC-analysis: 1,2,4-isomer: t_R = 17.30 min; 1,3,5-isomer t_R = 18.90 min. The observed spectroscopic data were corresponding to those reported in literature.

Catalytic cyclotrimerization of diphenylacetylene using 2.3.

The cyclotrimerization experiment was performed in an NMR tube equipped with a Teflon (Young) valve. A solution of **2.3** (0.03 mmol, 0.010 g) in C_6D_6 (0.6 mL) was made and diphenylacetylene (0.30 mmol, 0.053 g) was added. Then the tube was warmed at 80 °C. After 3 h at this temperature white crystals started to form in the tube, and after 24 h the amount of crystals had increased considerably. The tube was kept at this temperature for another 60 h after which the solid part was separated from the liquid by centrifuge. After washing with pentane (2x 1mL), white crystals of hexamethylbenzene were obtained in 71 % yield. The product was identified by GC-MS analysis (THF solvent).

X-ray crystal structure. Suitable crystals of **3.1**, **3.5** and **3.6** were mounted on top of a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream on a Bruker22 SMART APEX CCD diffractometer. The final unit cell was obtained from the xyz centroids of 9356 (**3.1**), 5597 (**3.5**) and 6591 (**3.6**) reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).[30] The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF[31] A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined. All refinement and geomatry calculations were performed with the program packages *SHELXL*[32] and *PLATON.*[33] Crystal data and details on data collection and refinement are presented in Table 5.

Table 5. Crystallographic data for **3.6**, **3.7** and **3.12**.

	3.6	***3.7***	***3.12***
chem formula	$C_{15}H_{30}NP_2V$	$C_{18}H_{28}NP_2V$	$C_{26}H_{48}N_4V_2$
Fw	337.30	371.32	518.56
crystal system	monoclinic	monoclinic	orthorhombic
color, habit	green, platelet	brown, block	red, platelet
size, mm	0.29 x 0.23 x 0.11	0.49 x 0.33 x 0.13	0.45 x 0.39 x 0.21
space group	$P2_1/c$	$P2_1/c$	$Pna2_1$
a, Å	15.1320(1)	10.404(1)	22.1898(12)
b, Å	8.9402(6)	10.939(1)	11.3749(6)
c, Å	13.7110(1)	17.404(2)	11.0225(6)
α, (°)	-	-	-
β, (°)	102.480(1)	95.317(2)	-
γ, (°)	-	-	-
V, Å^3	1811.0(2)	1972.2(3)	2782.2(3)
Z	4	4	4
ρ_{calc}, g.cm^{-3}	1.237	1.250	1.238
F(000)	720	784	1112
μ(Mo K$\overline{\alpha}$), cm^{-1}	7.14	6.62	5.37
temperature (K)	100(1)	100(1)	100(1)
θ range (°)	2.74, - 26.73	2.71 - 29.25	2.57 - 28.76
min and max transm	0.8116 – 0.9256	0.7005 – 0.9189	0.7227 – 0.8684
R(F)	0.0399	0.0470	0.0359
wR(F^2)	0.0950	0.1092	0.1803
GooF	1.021	1.042	1.014
observed reflns $F_o \geq 4.0\ \sigma\ (F_o)$)	3028	3837	6211
data collected (h, k, l)	-17:19; -10:11;-17:17	-13:13;-14:14;-22:23	-29:29;-15:12;-14:14
params refined	294	317	303

3.8 References

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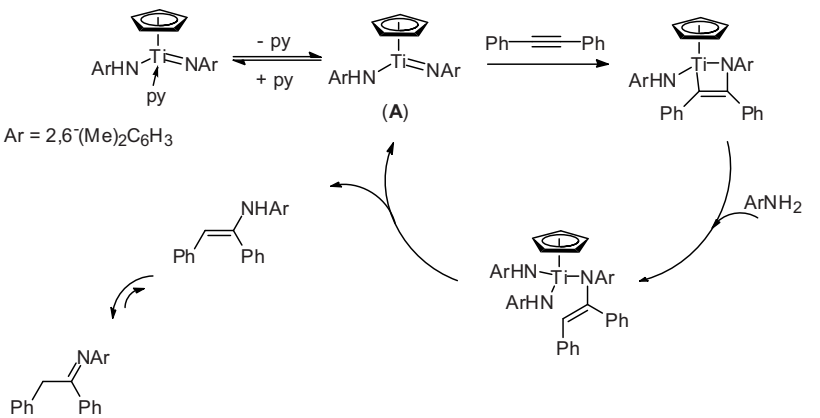
Chapter 4

Activity of vanadium(V) amido-imido species in catalytic C-N bond formation

*Treatment of the ionic species [Cp(i-Pr$_2$N)V(N-p-tolyl)][B(C$_6$F$_5$)$_4$] with 10 equiv of PhCCH or PhCCPh results in catalytic formation of substituted benzene derivatives. Cationic species of type [Cp(p-tolylNH)V(N-p-tolyl)]$^+$ could be generated upon treatment of [Cp(i-Pr$_2$N)V(N-p-tolyl)][B(C$_6$F$_5$)$_4$] and [Cp(i-Pr$_2$N)V(N-p-tolyl)][MeB(C$_6$F$_5$)$_3$] with an excess of p-toluidine. These complexes exhibit catalytic hydroamination activity toward terminal alkynes, generating Markovnikov products together with substituted quinoline co-product. This co-product results from a secondary reaction of the anti-Markovnikov product, which is consumed in the process. The anti-Markovnikov products could be observed when neutral vanadium chloride complex **2.7** was employed as hydroamination catalyst for terminal alkynes with t-BuNH$_2$.*

4.1 Introduction

In recent years, the catalytic addition of the N-H group of amines across unsaturated C-C bonds (hydroamination) has emerged as a powerful and atom-economic way to prepare more elaborate N-containing molecules. A wide range of catalysts are available for this reaction, based on late transition metals[1], lanthanides[2], actinides[3], alkali metals, alkaline earth metals[4] and early transition metals. Several research groups have developed group 4 metal complexes that can be used as catalysts for the hydroamination reaction.[5,6,7,8,9,10] Among these, the Cp_2TiMe_2 proved to be a particularly efficient (pre-)catalyst for this transformation. The active species in the hydroamination catalysis with this titanocene complex is proposed by Bergman to be the 16-electron monocyclopentadienyl titanium amido-imido compound CpTi(NHAr)(NAr) (**A**, Scheme 1) that is generated from the metallocene pre-catalyst by a cyclopentadienyl/amide exchange reaction in the presence of excess amine.

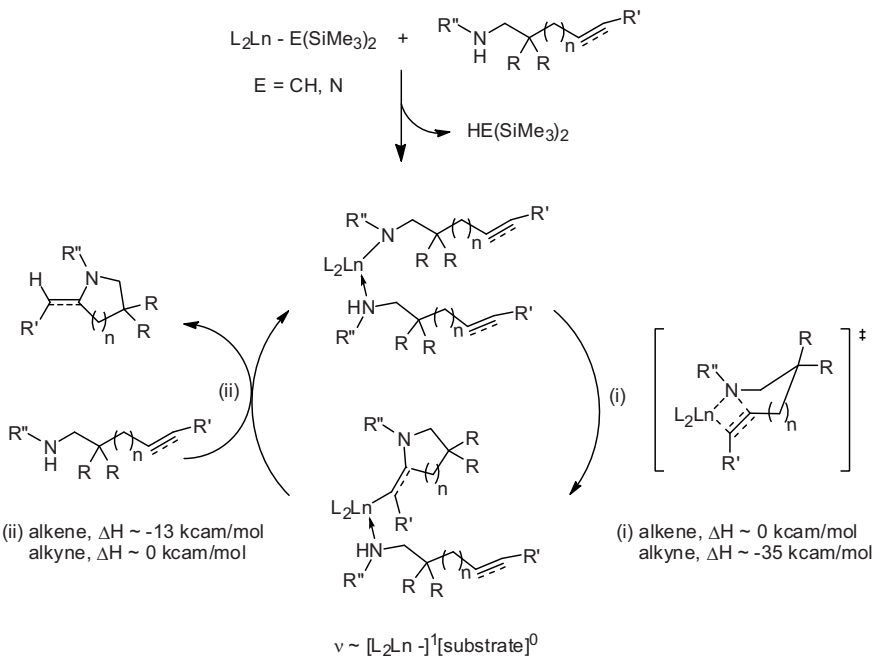


Scheme 1

Additional support for the intermediacy of such an amido-imido compound comes from quantum chemical calculations.[11] The most common mechanism proposed for this transformation when catalyzed by early transition metals involves a [2+2] cycloaddition of the unsaturated hydrocarbon with the metal-imido bond, followed

by protonation of the resulting metallacycle with a primary amine, regenerating the metal imido catalyst (Scheme 1).[5a]

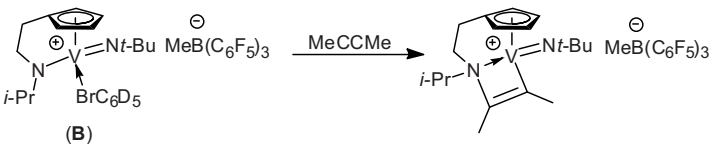
For complexes of this type, i.e. complexes that have a metal-amido and a metal-imido moiety, it is also possible to invoke an alternative mechanism in which the alkyne inserts into the Ti-N bond, followed by protonation of the resulting aminoalkenyl ligand. This is similar to the mechanism proposed for group 3 and lanthanide mediated intramolecular hydroamination/cyclization reactions of ω-alkenylamines (Scheme 2).[12] Recently this mechanism was also postulated for the hydroamination reaction using the group 4 metal catalyst, {η^5-$C_5Me_4SiMe_2N$(*t*-Bu)}$Zr(NMe_2)Cl$.[12d] Moreover, DFT calculation presented by Doye *et. al.*[13] showed that the energy profiles of the both pathways, [2+2] cycloadition and the insertion of the alkene into a Ti-N single bond, are very similar.



Scheme 2

For group 5 metals not much is known regarding this type of reactivity. Witte *et.al*[14] observations in the chemistry of the cationic cyclopentadienyl-amide vanadium imido complex [(η^5-$C_5H_4C_2H_4$N-*i*-Pr)V(N-*t*-Bu)(BrC_6H_5)][$MeB(C_6F_5)_3$]

(Scheme 3, **B**), show that the vanadium-imido bond appears to be inert towards unsaturated substrates, and that alkynes insert into the vanadium-nitrogen single bond (Scheme 3). Moreover, computational studies have shown that for the cationic vanadium amido-imido system the alkyne insertion into the vanadium-nitrogen single bond is thermodynamically favored.[15]



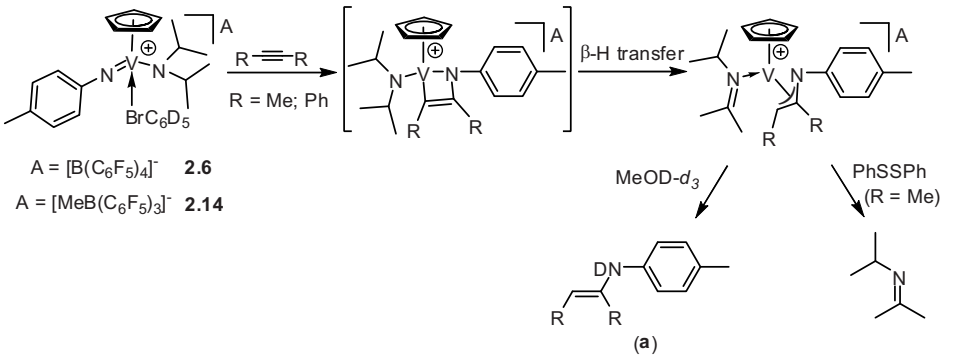
Scheme 3

Thus, the completely different behavior of the linked cyclopentadienyl-amido vanadium cation (**B**) [14b] versus that proposed for the isoelectronic titanium(IV) complex (**A**)[5c] towards unsaturated substrates kindled our interest in the relative reactivity of the metal-amido and metal-imido bond.

4.2 Reactivity of the cationic vanadium (V) amido-imido complexes towards alkynes

The synthesis of cationic vanadium(V) amido-imido species has been described in Chapter 2. Treatment of the ionic vanadium complexes [Cp(*i*-Pr$_2$N)V(N-*p*-tolyl)][B(C$_6$F$_5$)$_4$] (**2.6**) and [Cp(*i*-Pr$_2$N)V(N-*p*-tolyl)][MeB(C$_6$F$_5$)$_3$] (**2.14**) with 1 equivalent of alkyne, i.e. 2-butyne or diphenylacetylene, resulted in a dark red reaction mixtures. ^{1}H NMR spectroscopy revealed the formation of paramagnetic compound(s) that could not be readily identified. Attempts to isolate the paramagnetic vanadium cations were unsuccessful. The reaction mixtures were quenched with MeOD-d_3 and GC-MS analysis revealed the formation of deuterated *sec*-butylidene-*p*-tolylamine and N-(1,2-diphenylvinyl)-4-methylaniline (Scheme 4 - a). This suggests that the initially formed paramagnetic compound is the aza-allyl complex, [CpV(*p*-tolylNC(R)CHR)(N-*i*Pr$_2$)]$^+$ (Scheme 4), the result of a [2+2] cycloaddition reaction of the alkyne with the V=N bond, followed by an intramolecular proton transfer reaction. Formation of such a species is also

supported by the observation of the release of *N*-isopropyl-2-propanimine upon addition of PhSSPh to the reaction mixture of **2.14** with 2-butyne containing the paramagnetic species.[15] Unfortunately the remainder of the reaction mixture is intractable.



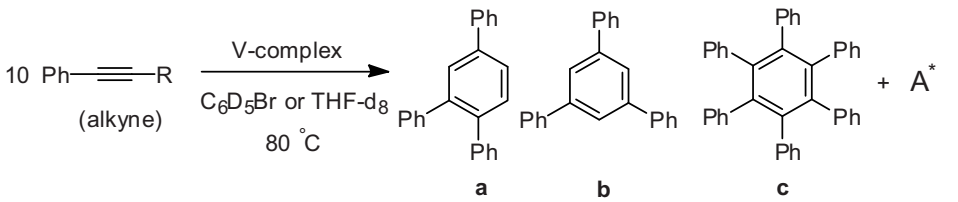
Scheme 4

Thus we have seen that cationic vanadium species **2.6** transforms into a paramagnetic species upon treatment with 1 equivalent of alkyne in a reaction initiated by cycloaddition of the alkyne with the V-imido bond. By increasing the amount of alkyne (i.e. diphenylacetylene, phenylacetylene) from 1 to 10 equivalents, cyclotrimerization products were obtained. Although metal-catalyzed cyclotrimerization of alkynes (or co-trimerization of alkynes and nitriles) to produce substituted benzenes (or pyridines) have been studied extensively,[16,17] this type of reactivity is new for cationic vanadium amido-imido species.

Upon treatment of **2.6** with phenylacetylene or diphenylacetylene in a 1:10 ratio vanadium:alkyne, the mixture become paramagnetic within 5 min from the alkyne addition. Further warming to 80 ºC generated the substituted benzene products (Table 1). The reactions were monitored by ^{1}H NMR spectroscopy. For phenylacetylene, full substrate consumption is observed in less than 2 h and GC/GC-MS confirmed the formation of the two cyclotrimerization isomers 1,2,4- and 1,3,5- triphenylbenzene (Table 1, entry 2). Also, the more sterically demanding substrate diphenylacetylene is converted into hexaphenylbenzene (C_6Ph_6) in 64 % isolated yield after 18 h at 80 ºC, in bromobenzene – d_5 (Table 1, entry 3 **c**). The Lewis base adduct [Cp(*i*-Pr$_2$N)V(N-*p*-tolyl)(thf)][B(C$_6$F$_5$)$_4$] (**2.5**) also converts

phenylacetylene into cyclotrimerization products within 20 h (Table 1, entry 1), indicating that the presence of Lewis base retards the activity of the catalytic species, but is not shutting it down completely. Apart from phenylacetylene cyclotrimerization products formed (entry 1 and 2), in the reaction mixture, 5 ~ 7 % of a tetrameric product (Mw = 416) was detected, plus traces of phenylacetylene dimers.

Table 1. *The cyclotrimerization reaction of phenylacetylene and diphenylacetylene with **2.5** and **2.6** vanadium species.*



entry	cat	R	time (h)	alkyne # conv(%)	yield (%)	product ratio
1	**2.5**	H	20	90	78[a]	**a**:**b** = 2.2:1
2	**2.6**	H	1.5	100	70[a]	**a**:**b** = 2:1
3	**2.6**	Ph	18	85	64[b]	**c**

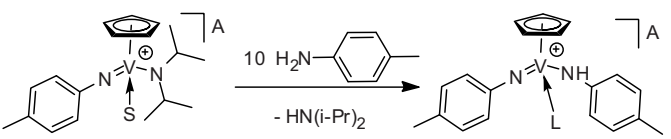
Reaction condition: 10 mol% cat and 10 equivalents of alkyne in bromobenzene-d_5 (entry 2 and 3) or THF-d_8 (entry 1) at 80 ºC. # Determined by ^{1}H NMR; [a] yield determined by GC analysis; [b] isolated yield; * paramagnetic species, *N*-isopropyl-2-propanimine and side products.

In comparison with the neutral system presented in Chapter 3 (section 3.4), the activity of the cationic species in these cyclotrimerization processes is higher, i.e. 10 equivalents of phenylacetylene/ 1 equivalent of **2.6** is converted within 1.5 h whereas the neutral system requires at least 18 h at 80 ºC to go to full conversion. The electronically unsaturated vanadium(III) cyclopentadienyl aza-allyl complex "[CpV(aza-allyl)]$^+$" presented in Scheme 2 (*vide supra*) could be the active species responsible for the catalysis observed for the cationic system.

4.3 Hydroamination studies with vanadium(V) amido-imido systems

4.3.1 Generation of cationic cyclopentadienyl vanadium (V) p-tolyl-amido-imido complexes

As mentioned in the introduction, important progress in the intermolecular hydroamination of alkynes was realized by Bergman using the neutral titanium complex [Cp(ArNH)(py)Ti=NAr].[5c] We were interested to see whether an isoelectronic cationic system based on vanadium shows catalytic activity for such hydroamination processes. Unfortunately, cationic vanadium complexes of the type Cp(*p*-tolylNH)V(N-*p*-tolyl)$^+$ were not available via direct routes (Chapter 2), as the selective introduction of the *p*-tolylNH group on the vanadium imido methyl complex was not successful. Thus, here an attempt to replace the N*i*-Pr_2 ligand in cationic vanadium systems **2.5**, **2.6** and **2.14** by NH(*p*-tolyl) is introduced. The cationic complex [Cp(*i*-Pr_2N)V(N-*p*-tolyl)(thf)][$B(C_6H_5)_4$] (**2.5**) was treated with an excess of *p*-toluidine at ambient temperature in THF-d_8. After 0.5 h at 80 ºC, the ^{1}H NMR spectrum of the crude mixture confirms the presence of free diisopropyl amine[18] and the formation of the Lewis base adduct cationic species **4.1** (δ Cp: 6.08 ppm, δ 3.61 ppm and 1.74 ppm coordinated THF[19]) (Scheme 5).



Scheme 5

On a preparative scale the Lewis base adduct **4.1** is obtained in a similar way followed by subsequent washing with hexane. Attempts to remove the final traces of free toluidine from the product resulted in gradual decomposition of the compound, however.

Analogously, cationic species [Cp(*i*-Pr_2N)V(N-*p*-tolyl)][$B(C_6F_5)_4$] (**2.6**) and [Cp(*i*-Pr_2N)V(N*p*-tolyl)][$MeB(C_6F_5)_3$] (**2.14**), upon treatment with an excess of *p*-toluidine in bromobenzene-d_5 solvent, are converted to the new vanadium species

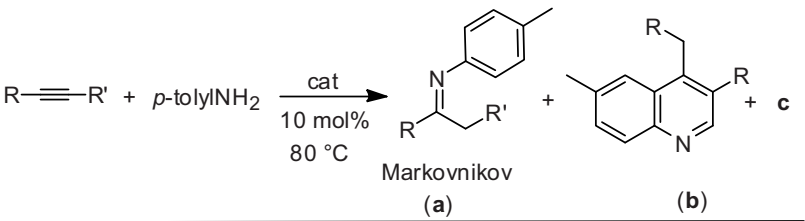
4.2 and **4.3** (Scheme 5) after 1 h at room temperature from the amine addition. The color of the reaction mixture changed from wine-red to crimson-red. ^{1}H NMR spectroscopy confirms the formation of the new species plus the presence of free diisopropyl amine[18]. The ^{19}F NMR spectrum of [Cp(*p*-tolylNH)V(N-*p*-tolyl)(*p*-tolylNH$_2$)][MeB(C$_6$F$_5$)$_3$] (**4.3**) in solution indicates a 80:20 mixture of solvent separated and contact ion pair ($\Delta\delta(F_m\text{-}F_p)$ = 2.64 ppm major species; contact ion pair ($\Delta\delta(F_m\text{-}F_p)$ = 6.4 ppm minor species respectively). These *p*-tolyl-amido-imido complexes **4.1**, **4.2** and **4.3** are stable in solution (THF-d$_8$ or C$_6$D$_5$Br) at 80 ºC for at least 2 weeks.

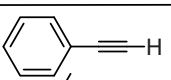
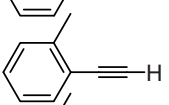
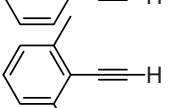
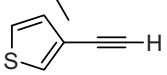
4.3.2 Hydroamination catalysis by cationic cyclopentadienyl vanadium(V) amido-imido complexes

To investigate the catalytic activity of the cationic vanadium species described in the previous section in intermolecular hydroamination processes, and get a look at the relative reactivity of V-N vs. V=N bonds, a wide range of mono- and disubstituted alkyne substrates were used, with *p*-toluidine as the amine. Prior to alkyne addition, the cationic vanadium(V) complexes **2.5**, **2.6** and **2.14** were pretreated with an excess of *p*-toluidine, resulting in conversion to the vanadium *p*-tolylamido-imido cations **4.1**, **4.2** and **4.3** generated *in situ*. The hydroamination reactions were performed for terminal and internal alkynes with *p*-toluidine in a ratio 1:1, involving a catalytic amount of 10 mol % of vanadium species. The reactions were carried out in bromobenzene-d_5 at 80 ºC and monitored by ^{1}H NMR spectroscopy. Although, complex **4.1** was treated with several substrates (phenylacetylene, 1-hexyne and 2-butyne) at elevated temperatures (80 ºC) and for prolonged time (2 weeks), no activity was observed, most probably due to the presence of the hard Lewis base THF.

The activity of catalyst **4.2** was investigated toward internal and terminal, aliphatic and aromatic alkyne substrates and the results are presented in Table 2.

Table 2. *Intermolecular hydroamination of different alkynes and p-toluidine in 1:1 ratios using cationic vanadium **4.2**.*



entry	cat.	alkyne (RCCR')	time (h)	conversion (%)#		yield (%)*		
				alkyne	*p*-toluidine	**a**	**b**	**c**
1	**4.2**		24	90	70	47	20	3
2	**4.2**		72	65	50	40	9	4
3	**4.2**		264	50	50	50	-	-
4	**4.2**		48	80	60	50	10[i]	16
5	**4.2**	nBu—≡—H	120	80	75	58	16	4[ii]
6	**4.2**	Me—≡—Me	144	40	35	30	5[iii]	< 4
7	**4.2**	Ph—≡—Me	144	30	30	30	-	-

Reaction condition: 10 mol % cat, 10 equiv of alkyne to 10 equiv of *p*-toluidine (1:1 ratio) in bromobenzene-d_5 at 80 ºC and '**c**' is alkyne cyclotrimerization product; # determined by ^{1}H NMR analysis using internal standard; * the major products determined by gas chromatography (GC) with an internal standard (cyclooctane or cyclohexane); [i] linear eneimine Mw = 323, two isomers (t_R = 19.0 min, t_R = 19.5 min) were observed; [ii] a mixture of two isomers of 1-hexyne tetramers (Mw=353, t_R = 16.8 and 17.0 min), was obtained; [iii] for 2 -butyne the linear eneimine, a reaction product of two alkynes and one amine (Mw = 215), is observed.

The data indicate that internal alkynes are poor substrates for vanadium system **4.2**, whereas the terminal alkynes prove to be more effective. The isolated products of alkyne hydroamination with *p*-toluidine are exclusively the imines resulting from Markovnikov addition of the amine to the alkyne. Nevertheless, a side product is also formed (*vide infra*). The results presented in Table 2 indicate that vanadium species **4.2** is a relatively slow catalyst compared to its titanium counterpart of

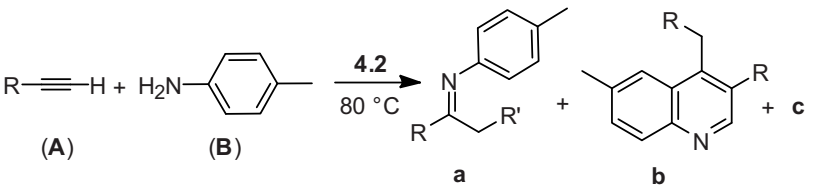
Bergman *et. al*[5c], which rapidly catalyses the addition of 2,6-dimethylaniline to diphenylacetylene (75 ºC, $t_{½}$ < 15 min, 95 % yield). When the cyclopentadienyl titanium (pre-)catalyst Cp_2TiMe_2 is used as catalyst for terminal alkynes a mixture of Markovnikov/*anti*-Markovnikov products is obtained.[6e,7h,20]

Although less efficient than for terminal alkynes, vanadium species **4.2** is also able to effect hydroamination of some *internal* alkynes (2-butyne and 1-phenyl-propyne). Towards diphenylacetylene and 3-hexyne it shows no activity. As mentioned above, the hydroamination of phenylacetylene with p-toluidine by **4.2** produces, in addition to the Markovnikov hydroamination product (**a**), a side product that was identified as a substituted quinoline (**b**). The formation of quinoline products is new for vanadium-based hydroamination systems.

Apart from the Markovnikov hydroamination product and the substituted quinoline, other minor side products are observed. These are mainly acetylene cyclotrimerization products (**c**), although for 1-hexyne no cyclotrimerization products are observed; instead products with a mass of tetramers are formed.[21] Also in case of phenylacetylene ca. 6 % of tetramer (Mw = 414, t_R = 25.7 min) could be detected and ca. 5 % of phenylacetylene dimer (Mw = 206, t_R = 13.0 min).[22] Entry 4 shows the highest amount of substituted benzene products plus dimer (Mw = 218, t_R = 13.1 min, ca. 4 %). Upon increasing the steric hindrance of the phenylacetylene (by introducing methyl substituents on the *ortho* positions) the amount of substituted quinoline (**b**) can be partly (entry 2) or completely suppressed (entry 3). In the latter, formation of oligomers is also absent, although for the *o*-tolyl substrate still 10 % dimer (Mw = 234, t_R = 15.6 min)[23] is formed. From the data presented in Table 2 it is clear that formation of the quinoline product consumes 2 equiv of acetylene for 1 equiv of amine. To see whether the production of substituted quinolines can be increased, several experiments were conducted with increasing amounts of alkyne (Table 3) and the reactions were monitored by ^{1}H NMR spectroscopy. By increasing the phenylacetylene : *p*-toluidine ratio from 1:1 to 2:1, the amount of quinoline product (**b**) is increased, but the amount of alkyne cyclotrimerization products also increases by a factor of 4 (Table 3, entry 1 and 2). Going to an even higher alkyne to amine ratio of 3:1

(Table 3, entry 3) slightly increased the absolute amount of product **a** and **b**, but significantly increased the amount of cyclotrimerization product.[24] The increase in alkyne concentration appears to slow down the overall conversion. The prolonged reaction time increased the number of side reactions.

Table 3. *Intermolecular hydroamination results with different alkynes: p-toluidine ratios using cationic vanadium **4.2** as catalyst.*



entry	R	ratio (**A** : ***B***)	time (h)	alkyne conv(%)	μmol *		
					a	**b**	**c**
1	Ph	1 :1	24	90	160	68	10
2	Ph	2 :1	120	80	168	210	45
3	Ph	3 :1	216	70	180	220	140
4	*n*-Bu	1 :1	120	82	195	70	25
5	*n*-Bu	2 :1	192	80	395	90	30

The reactions were performed with 10 mol % (0.034 mmol entry 1-3; 0.036 mmol entry 4-5) **4.2** vanadium catalyst, in bromobenzene-d_5 at 80 ºC. * Major products determined by gas chromatography (GC) analysis versus cyclooctane as internal standard; 'c' is accounted for substituted benzene product for entry 1, 2, 3 and for tetramer products (Mw = 353, two isomers t_R = 16.8 and 17.0 min) for entry 4 and 5. Compounds with Mw = 271 (entry 4-5, two isomers t_R = 14.3 and 14.5 min) and oligomers with Mw=517 (n=6, two isomers, t_R = 19.5 and 20.4 min) are observed also.

Using 1-hexyne, the major product observed is the Markovnikov hydroamination product together with amounts of quinoline product **b** and products with a mass of 1-hexyne tetramers (Table 3 entry 4, two isomers). Increasing the amount of 1-hexyne versus *p*-toluidine (Table 3, entry 5) did not significantly increased the amount of **b** and the tetramers (Mw = 353, two isomers t_R = 16.8 min and t_R = 17.0 min), but instead leads to an increase in hydroamination product; higher molecular mass oligomers (Mw = 517, two isomers t_R = 19.5 and t_R = 20.4 min) are observed also.

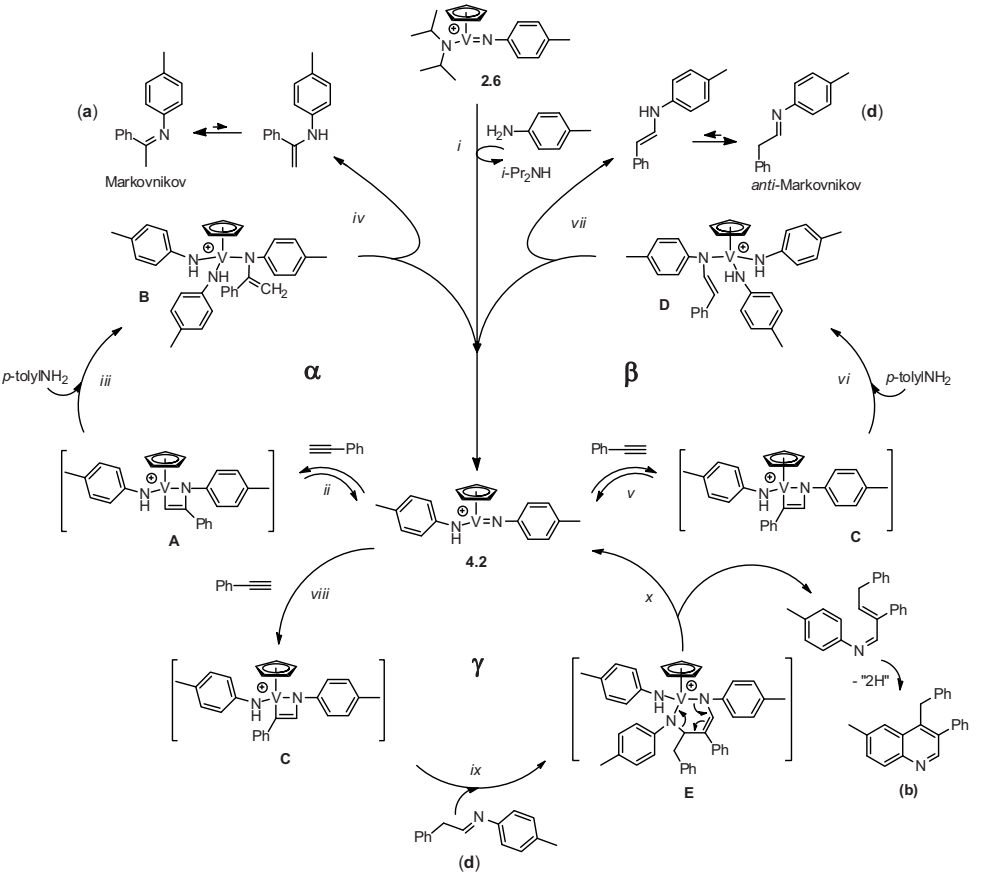
The substituted quinoline (**b**) derived from phenylacetylene was produced on preparative scale, under conditions similar to the NMR tube experiment, by using a 2:1 ratio of phenylacetylene : *p*-toluidine in the presence of 10 mol % of **4.2**. To separate **b** from the other products, the reaction mixture was first separated by column chromatography, followed by preparative HPLC or by preparative-GC. The ^{1}H, ^{13}C NMR spectroscopic and MS data of the material obtained are consistent with the proposed nature of the substituted quinoline.

A plausible reactive pathway leading to the formation of the hydroamination product (**a**) and the substituted quinoline (**b**) in the case of phenylacetylene is presented in Scheme 6, which summarizes the various catalytic pathways. In the first step, the cationic vanadium amido-imido complex **4.2** is generated from the **2.6** by ligand exchange with an excess of *p*-toluidine (pathway (*i*)). Then **4.2** undergoes a [2+2] cycloaddition reaction with phenylacetylene, forming the azavanadacyclobutene intermediate **A** and **C** that differ in regioselectivity of the cycloaddition (pathways (*ii*) and (*v*)). The metallacycles **A** and **C** are then protonated by amine (pathway *iii* and *vi* respectively) to generate the tris(amido)vanadium intermediates **B** and **D**. α-H elimination then liberates the enamine product that tautomerizes to the thermodynamically stable imine (generating, via pathway (*iv*) the Markovnikov product **a** and via pathway (*vii*) the *anti*-Markovnikov product **d**) and regenerating the catalyst **4.2**.

The substituted quinoline product (**b**) is formed by insertion of the *anti*-Markovnikov product (pathway (*ix*)) into the azametallacyclobutene complex **C** to form a six membered ring metallacycle intermediate (**E**), which can perform a [4 + 2] retrocycloaddition to regenerate the **4.2** and extrude an *α, β*- unsaturated imine. This linear eneimine leads to the quinoline product (**b**) via a cyclization process that involves activation of an *o*-CH bond of the *p*-tolyl group. Although the fate of the two H-atoms that are eliminated in this process is not clear as yet,[25] there is precedent for this ring-closure.[26,27]

Hence, the catalytic process can be divided into three sub-cycles: (1) cycle α - generation of the Markovnikov product, (2) cycle β - generation of the *anti*-Markovnikov product and (3) cycle γ - generation of the substituted quinoline

product. Apparently, during the hydroamination process in the presence of **4.2**, both Markovnikov and *anti*-Markovnikov products are formed, but the latter reacts further by insertion into V-C bond, generating a new C-N organic species.



Scheme 6

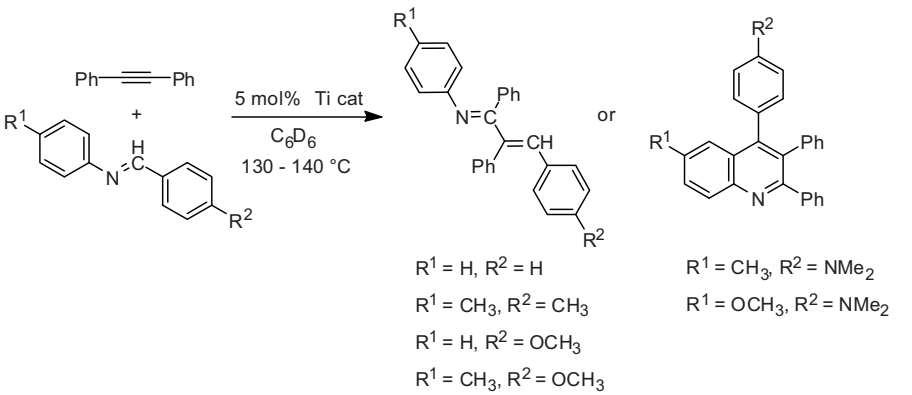
Using steric hindered alkynes (Table 2, entry 2 and 3) β-cycle is blocked preventing the formation of the *anti*-Markovnikov product, and therefore of the quinoline product. This suggests that sterically hindered alkynes make intermediate **C** either inaccessible or inert towards protonation. In the latter case, the life time of **C** is dependent on the rate of the retro-cycloaddition liberating the substrate and **4.2**.

Increasing the alkyne : amine ratio influences the amount of substituted quinoline product formed, and at higher alkyne concentrations (Table 3, entry 1, 2 and 3) the formation of cyclotrimerization products is enhanced also. Employing 1-hexyne, the formation of the Markovnikov product (**a**) is the favored path (cycle α), and only a small amount of substituted quinoline type product was observed together with formation of higher molecular mass tetramers; no trimerization occurred. Doubling the amount of 1-hexyne doubled the amount of the Markovnikov product formed. However, no increase of the substituted quinoline product was recorded. In all hydroamination reactions the amine has been not fully converted. Since the quinoline product **b** can be obtained only via insertion of the *anti*-Markovnikov product (**d**), the ratio between the products **a** and **b** is an indication of the regioselectivity achieved in the hydroamination process. An explanation for the increase of quinoline product formation upon increasing the alkyne concentration could be found in the relative rates of formation of **A** and **C**. If the backward reaction of **C** to **4.2** is faster than the rate of insertion, the formation of *anti*-Markovnikov product is retarded. Increasing the alkyne concentration changes the overall k value of the reaction in favor of the intermediate **C** facilitating the generation of the *anti*-Markovnikov product.

To see whether changing the activating agent from borate to borane has any significance for the hydroamination process, several alkynes (phenylacetylene, 2-butyne and 1-hexyne) and *p*-toluidine were investigated in the presence of the [Cp(*p*-tolylNH)V(N-*p*-tolyl)(*p*-tolylNH$_2$)][MeB(C$_6$F$_5$)$_3$] (**4.3**) as catalyst. The reactions were performed under the same conditions as for **4.2**. The results obtained with the **4.3** catalytic system displays the same products pattern as with **4.2** (Table 2) suggesting that the difference in counterion does not have a significant effect on the process.

The formation of such a substituted quinoline-type compound was reported previously by Mindiola *et.al*[27] who obtained the triaryl-substituted quinolines from catalytic carboamination reactions of aldimines with diphenylacetylene using a titanium complex [(nacnac)Ti=NAr(FC$_6$H$_5$)][B(C$_6$F$_5$)] (nacnac = (ArNC(*t*-Bu)$_2$)CH, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) as catalyst (Scheme 7). The titanium species showed

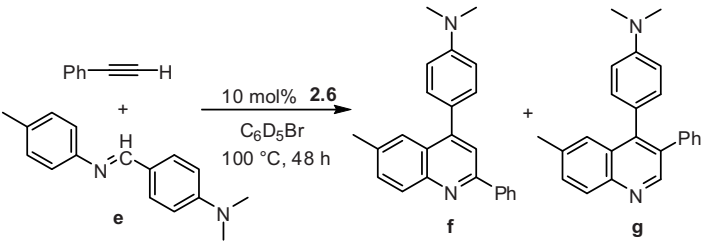
higher activity toward electron-rich *p*-aryl-substituted substrates to afford *α,β*-unsaturated imines (eneimine)[28] or quinoline products.



Scheme 7

The substituted quinoline products were obtained when electron rich α,*β*-unsaturated imines with R^1 = CH_3, R^2 =NMe_2 and R^1 = OCH_3, R^2 =NMe_2 were used.

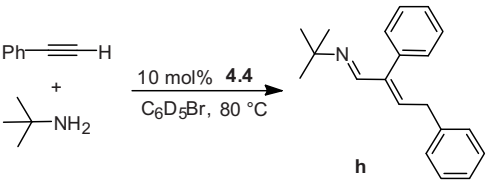
On the basis of this work, we checked whether **2.6** could also perform such a carboamination. Hence, the carboamination reaction of phenylacetylene and the aldimine **e** (ratio 1.5:1) was performed in the presence of 10 mol % of **2.6** in bromobenzene-d_5 at 100 ºC for 48 h. Based on ^{1}H NMR spectroscopic data 45 % of the starting material was converted and the CG/GC-MS analyses indicate formation of two isomers of the substituted quinoline as major products (Scheme 8): isomers **f** and **g** in a ratio 0.22:1 respectively, plus traces of phenylacetylene cyclotrimerization products. ^{1}H NMR spectroscopic analysis and GC-MS also showed the presence of free diisopropyl amine, resulting from catalyst generation. It is presently unclear where the two H-atoms go that are lost upon forming the quinoline. Neither styrene nor ethylbenzene (possible reduction products of phenylacetylene) were observed, nor was evidence found for the formation of H_2. No comments were made on this point by Mindiola in his research on quinoline formation.[27]



Scheme 8

The formation of the products **f** and **g** fits within the catalytic cycle presented in Scheme 5 (*vide supra*) and supports the generation of ring annulated systems, (quinolines) during the hydroamination of phenylacetylene with *p*-toluidine.

To see whether changing the amine makes a difference in the hydroamination process, the conversion of an alkylamine (*in casu* *t*-$BuNH_2$) with phenylacetylene was investigated. Therefore, the cationic species **2.14** was treated with an excess of *t*-$BuNH_2$ (10 equivalents/1 equivalent vanadium) generating the *t*-butyl amido, *p*-tolylimido compound Cp(*t*-BuNH)V(N-*p*-tolyl)[$MeB(C_6F_5)_3$] (**4.4**) with concomitant liberation of diisopropyl amine. The retention of the *p*-tolylimido group in **4.4** is also evident from the absence of free *p*-toluidine in the ^1H NMR spectrum of the mixture. The ^{19}F NMR spectrum of Cp(*t*-BuNH)V(N-*p*-tolyl)[$MeB(C_6F_5)_3$] (**4.4**) indicates an approximate 80:20 mixture of solvent separated and contact ion pair species ($\Delta\delta(F_m\text{-}F_p)$ = 2.64 ppm for the solvent-separated ion pair, $\Delta\delta(F_m\text{-}F_p)$ = 6.45 ppm for the contact ion pair). After addition of phenylacetylene and warming of the reaction mixture over 2 h at 80 ºC, all of the phenylacetylene was consumed. The ^1H NMR spectroscopy and GC-MS analysis of the reaction mixture indicated the formation of the enimine **h** (Mw = 277, 76 % ^1H NMR internal standard) as the only product from the catalysis (Scheme 9). Simple hydroamination products and phenylacetylene cyclotrimerization products could not be detected. Instead the GC-MS analysis revealed the formation of a small amount of the Markovnikov hydroamination product of phenylacetylene with *p*-tolylamine, resulting from initial [2+2] cycloaddition of phenylacetylene with the V=N-*p*-tolyl bond in the catalyst.



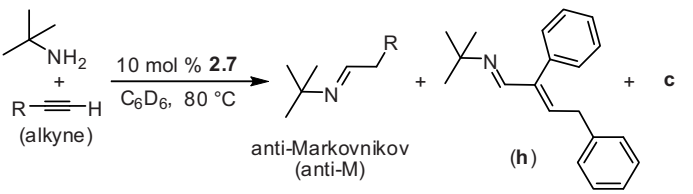
Scheme 9

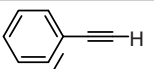
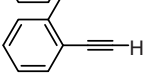
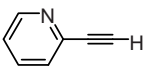
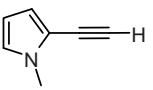
The formation of product **h** follows the same pathway as described for the initial stages of the formation of substituted quinoline from phenylacetylene and *p*-tolylamine by vanadium species **4.2** (Scheme 6, cycle γ), with the exception that the *α, β*-unsaturated imine formed does not perform a subsequent ring closure (due to the absence of an aryl substituent on nitrogen). Apparently, cationic species **4.4** generates selectively the *anti*-Markovnikov hydroamination product, which is then consumed by insertion into the azametallacycle intermediate, previously formed by [2+2] cycloaddition of phenylacetylene to the V=N-*t*-Bu bond, generating product **h**. It indicates that the hydroamination of phenylacetylene with *t*-butylamine by **4.4** has a high *anti*-Markovnikov selectivity.

4.3.3 Hydroamination catalysis by neutral vanadium(V) amido-imido complexes

The results obtained with the cationic **4.4** system (*vide supra*) kindled our interest in the reactivity of neutral *t*-Bu-amido-imido vanadium complexes. Since the neutral vanadium methyl complex Cp(*t*-BuNH)V(N-*t*-Bu)Me (**2.1**) could not be obtained in pure form, hydroamination reactions were performed in the presence of neutral chloride compound Cp(*t*-BuNH)V(N-*t*-Bu)Cl (**2.7**). To our surprise, the (formally 18 v.e.) neutral vanadium chloride shows catalytic activity in the hydroamination of terminal alkynes, and at a faster rate than the cationic species (Table 4). The hydroamination reactions were performed using several internal and terminal alkynes in the presence of 10 mol % of **2.7**. All reactions were carried out in benzene-d_6 at 80 ºC, in a 1:1 ratio alkyne:amine and were monitored by ^{1}H NMR spectroscopy.

Table 4. *Intermolecular hydroamination results of terminal alkyne and t-BuNH$_2$ in the presence of neutral vanadium complex **2.7**.*



entry	alkyne	time (h)	alkyne conv (%)#	conv (%)# anti-M	h	c*
1		16	100	70	27	< 2
2		48	77	72	2	3
3	*n*Bu—≡—H	48	98	96	-	2
4		3	60	58	-	2
5		18	60	35	-	25

Reaction conditions: 34 μmol of **2.7** cat, 10 equiv alkyne and p-toluidine (1:1 ratio) in benzene-d_6 at 80 ºC; # determined by ^{1}H NMR analysis using internal standard; * alkyne cyclotrimerization side product as determined by GC.

Reaction of phenylacetylene with *t*-BuNH$_2$ in the presence of **2.7** gives the *anti*-Markovnikov hydroamination product together with the eneimine **h** in an 8:1 ratio (Table 4, entry 1). The reaction was run to full conversion of the phenylacetylene. The formation of the organic products was established by ^{1}H NMR and GC/GC-MS analyses. In addition to the *anti*-Markovnikov and eneimine products, alkyne cyclotrimerization products were detected as well, although in small amounts (< 2% in total). Comparable hydroamination product formation was observed for 2-Me-PhCCH substrate (entry 2), albeit at slow conversion (after 48 h at 80 ºC, 23 % of the starting material is still present), and the amount of eneimine is substantially reduced. The *anti*-Markovnikov product was formed highly selectively with the aliphatic alkyne substrate 1-hexyne, and the starting material was fully converted within 48 h 80 ºC. The *N*-methylpyrrolyl-acetylene substrate produced the highest

amount of alkyne trimerization side product (25 %). Several internal alkynes (*e.g.* 3-hexyne, 1-phenylpropyne) were investigated as substrates, but no activity was observed. The high activity of the neutral catalyst system **2.7** is remarkable, and it is unlikely that **2.7** itself is the active species. Nevertheless, no conclusive evidence could be obtained as to the nature of the actual active species; *e.g.* CpH (which could be produced upon protonolysis of the Cp-V bond, leading to a non-Cp catalyst species) could not be detected.

The neutral *p*-tolylimido species Cp(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**2.9**) and Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**) show no activity in the hydroamination reaction of terminal alkyne (phenylacetylene, 1-hexyne) and *p*-toluidine even after prolonged reaction time of 8 days at 80 ºC. ^{1}H NMR spectroscopy reveals the presence of *N*-isopropyl-2-propanimine and methane in the hydroamination mixture with **2.3** (10 mol %) suggesting that catalyst thermolysis is taking place. The only products observed that could stem from catalysts were traces of the cyclotrimers of phenylacetylene. A similar result was obtained when *t*-$BuNH_2$ and phenylacetylene were employed in hydroamination reaction in the presence of 10 mol % of **2.3**. Treatment of phenylacetylene and *p*-toluidine with **2.9** (10 mol %) for 7 days at 80 ºC, shows in the ^{1}H NMR spectrum only the presence of diisopropyl amine together with the vanadium (IV) dimer $[CpV(\mu\text{-}p\text{-tolylN})Cl]_2$[29] plus traces of substituted benzenes. Also, when using the neutral vanadium methyl complex Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) for hydroamination of *t*-$BuNH_2$ and phenylacetylene (1:1 ratio), the hydroamination product is not observed, instead the vanadium(IV) dimer $[CpV(\mu\text{-}t\text{BuHN})t\text{-BuN}]_2$ (**3.12**) is formed (full characterization in Chapter 3). Thus it seems that the presence of both chloride and the use of *t*-$BuNH_2$ is required for the neutral catalyst system to be effective. Further research would be required to elucidate the true nature of this catalysis.

4.4 Concluding remarks

Whereas for the cationic constrained geometry vanadium imido complex [(η^5-$C_5H_4C_2H_4N$-*i*-Pr)V(N-*t*-Bu)(BrC_6H_5)][$MeB(C_6F_5)_3$] insertion of unsaturated alkynes occurs at the vanadium-nitrogen single bond, in the half-sandwhich vanadium complexes **2.5** and **2.6** the insertion of the C-C unsaturated bond takes place into the vanadium-nitrogen double bond. Addition of the *p*-toluidine to the **2.5** and **2.6** displaced the diispropylamido ligand generating the vanadium *p*-tolyl-amido-imido cationic species [Cp(*p*-tolylNH)V(N*p*-tolyl)]$^+$ **4.1** and **4.2**. The latter cationic species shows catalytic activity in intermolecular hydroamination reactions generating a mixture of Markovnikov and substituted quinoline products. The substituted quinoline is most probably obtained by insertion of the *anti*-Markovnikov product (aldimine) into the azametallacyclobutene intermediate, generated from a [2+2] cycloaddition of phenylacetylene with V=N bond. Displacement of the diispropylamido ligand in **2.6** was achieved by *t*-$BuNH_2$ also generating **4.4** species, which in hydroamination reaction generates exclusively the alkylated α,β – unsatutared imine compound **h** and no formation of simple hydroamination products. Surprisingly, the neutral vanadium complex **2.7** proved to be more reactive than the cationic catalysts in generating the *anti*-Markovnikov hydroamination product.

4.5 Experimental section

General considerations. General synthetic and handling techniques and solvent purification have been given in previous chapters. Reagents were purchased from commercial suppliers and used as received, unless stated otherwise. 1-Phenyl-1-propyne (distilled over CaH_2) was purchased from Aldrich and dried before used as recommended.[30] 1-Alkynes (Merck) were brought in a flask containing freshly ground CaH_2 and stirred at room temperature for at least 24 h.[30] Subsequent vacuum transfer and passage through a plug of neutral alumina afforded colorless oils which were stored immediately at -30 °C under nitrogen. The hydroamination experiments were conducted in NMR tubes equipped with a Teflon valve (Young). GC analyses were performed on a HP 6890 instrument with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. The Markovnikov hydroamination products of phenylacetylene and 2-butyne with *p*-toluidine were synthesized separately (to serve as reference) according to literature procedures.[31] The generation of compounds **2.5**, **2.6**, **2.7** and **2.14** was reported in Chapter 2.

Reaction of [Cp(*i*-Pr$_2$N)V(N-*p*-tolyl)][MeB(C$_6$F$_5$)$_3$] (2.14) with MeCCMe.

Compound **2.14** was generated by addition of bromobenzene-d_5 (0.5 mL) to a mixture of **2.3** (0.010 g, 0.030 mmol) and $B(C_6F_5)_3$ (0.014 g mg, 0.030 mmol). The solution was attached to a vacuum line and frozen in liquid nitrogen. Via a calibrated gas bulb, 29 mmHg (0.030 mmol) of 2-butyne was condensed in. The tube was closed and thawed and the reaction mixture was analyzed by ^{1}H NMR spectroscopy, revealing formation of a paramagnetic compound. ^{1}H NMR (400 MHz, C_6D_5Br, 25 °C): δ 73.3 (br, $\Delta\nu_{1/2}$ = 3500 Hz), 57.4 (br, $\Delta\nu_{1/2}$ = 4000 Hz), 30.4 (br, $\Delta\nu_{1/2}$ = 120 Hz), -15.5 (br, $\Delta\nu_{1/2}$ = 340 Hz). ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 °C): δ -130.0 (br, *o*-C_6F_5), -163.0 (br, *p*-C_6F_5), -164.6 (br, m-C_6F_5). The resulting solution was treated with methanol-d_4 and analyzed by GC-MS analysis, revealing the formation of *sec*-butylidene-*p*-tolylamine-*dn* (n = 1 – 4). The same procedure was applied when using the THF adduct of the cationic vanadium system, **2.5** and the Lewis base-free **2.6**.

Reaction of [Cp(*i*-Pr$_2$N)V(N-*p*-tolyl)][B(C$_6$F$_5$)$_4$] with PhCCPh.

To a solution of **2.6** (ca. 0.03 mmol) in C_6D_5Br (0.6 mL) prepared in an NMR tube (equipped with a Teflon Young valve) as described in Chapter 2, PhCCPh (5 mg, 0.03 mmol) was added. ^{1}H NMR spectroscopy analysis revealed formation of a paramagnetic compound. ^{1}H NMR (400 MHz, C_6D_5Br, 25 °C): 15.19 (br, $\Delta\nu_{1/2}$ = 384 Hz), 9.99 (br, $\Delta\nu_{1/2}$ = 251 Hz), 7.95 (br, $\Delta\nu_{1/2}$ = 167 Hz), - 0.48 (br, $\Delta\nu_{1/2}$ = 82 Hz), -2.56 (br, $\Delta\nu_{1/2}$ = 120 Hz), -10.97 (br, $\Delta\nu_{1/2}$ = 160 Hz). ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ -132.39 (s, *o*-F, B(C_6F_5)$_4$), - 162.95 (s, *p*-F, B(C_6F_5)$_4$), -165.90 (s, *m*-F, B(C_6F_5)$_4$). The resulting solution was treated with methanol-d_4 and analyzed by GC-MS analysis, revealing the formation of deuterated *N*-(1,2-diphenylethylidene)-4-methylaniline.

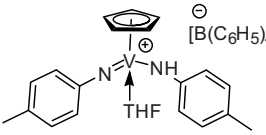
Catalytic cyclotrimerization of phenylacetylene using vanadium complexes 2.5 and 2.6.

The cyclotrimerization experiments of phenylacetylene in the presence of cationic vanadium species **2.5** and **2.6** were performed on NMR-scale using an NMR tube with Teflon (Young) valve. The cationic species were freshly generated, to which the PhCCH (10 equiv/1 equiv vanadium) was added. The experimental procedure was followed as previously described in Chapter 3.

Catalytic cyclotrimerization of diphenylacetylene using 2.6.

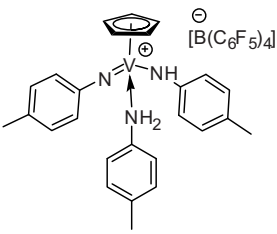
The cyclotrimerization experiment was performed in an NMR tube equipped with a Teflon (Young) valve. To a freshly prepared solution of **2.6** (0.03 mmol, 0.010 g) in 0.6 mL C_6D_5Br, 10 equivalents of diphenylacetylene (0.30 mmol, 0.053 g) were added. The tube was warmed at 80 °C for 18 h. The experimental procedure was followed as previously described in Chapter 3.

Generation of [Cp(*p*-tolylNH)V(N-*p*-tolyl)(thf)(*p*-tolylNH$_2$)][B(C$_6$H$_5$)$_4$] (4.1)



To a warm solution (50 °C) of **2.5**[32] (0.09 g, 0.13 mmol) in 3 mL THF, *p*-toluidine (0.29 g, 2.69 mmol) was added. The reaction mixture was warmed to 70 °C and stirred for 0.5 h. The color changed from red-orange to red-brown. The solvent was evaporated under reduced pressure, and the crude product was washed with pentane (3 x 3 mL). Removal *in vacuo* of residual pentane gave [Cp(*p*-tolylNH)V$^+$(N-*p*-tolyl)(THF)][B(C$_6$H$_5$)$_4$]$^-$ (**4.1**) as a brown-red powder that also contained 1 equiv of *p*-toluidine (seen as free amine by NMR in THF-d$_8$ solvent). ^{1}H NMR (400 MHz, THF-d$_8$ 25 ºC): δ 14.10 (s broad, 1H, NH), 7.31 (broad m, 4H BPh$_4$), 7.22 (m, 4H BPh$_4$), 7.07 ~ 6.98 (m, 10H BPh$_4$ and *p*-tolyl), 6.89 ~ 6.83 (m, 10H BPh$_4$, *p*-tolyl and *p*-toluidine), 6.68 (t, *J* = 7.15Hz 2H), 6.56 (d, *J* = 8.31 Hz, 2H *p*-toluidine), 6.43 (broad s, 1H, NH *p*-toluidine), 6.08 (s, 5H, Cp), 4.34 (broad, NH *p*-toluidine), 2.29 (s, 3H Me *p*-tolyl), 2.19 (s, 3H Me *p*-tolyl), 2.14 (s, 3H, Me *p*-toluidine). ^{13}C {^{1}H}NMR (125 MHz, THF-d$_8$, 25 ºC): δ 146.79 (*ipso*-C, *p*-toluidine), 145.83(*ipso*-C *p*-tolyl), 140.79 (*ipso*-C *p*-tolyl), 131.29 (CH *p*-toluidine), 131.24 (CH *p*-tolyl), 130.95 (*ipso*-C *p*-tolyl), 129.71 (CH *p*-tolyl), 129.34 (CH *p*-tolyl), 127.60 (CH *p*-tolyl), 127.4z1 (*ipso*-C *p*-tolyl), 116.59 (CH, *p*-toluidine), 112.11 (CH, Cp), 22.49 (CH, Me *p*-tolyl), 21.95 (CH, Me *p*-tolyl), 21.86 (CH, Me *p*-toluidine). ^{51}V NMR (131 MHz, THF-d$_8$, 25 °C, VOCl$_3$ external standard): δ -612.51 (broad).

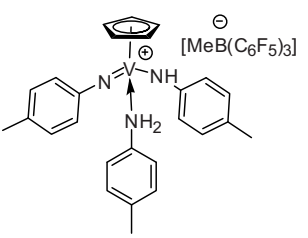
Generation of [(*p*-tolylNH)CpV(N*p*-tolyl)(*p*-tolylNH$_2$)][B(C$_6$F$_5$)$_4$] (4.2)



p-Toluidine (0.08 g, 0.77 mmol) was added to a freshly prepared solution of **2.6**[32] (0.03 g, 0.09 mmol) in 0.6 mL C$_6$D$_5$Br (NMR tube reaction). After 1h at ambient temperature the solvent and volatiles were removed *in vacuo* and the remaining residue was washed with pentane (2 x 0.5 mL). Removal *in vacuo* of residual pentane gave a red foam that turned into an oil upon standing. ^{1}H NMR spectroscopy of the red oil confirmed the presence of cationic species **4.2**. ^{1}H NMR (400 MHz, C$_6$D$_5$Br , 25 ºC): δ 12.77 (s broad, 1H, NH), 7.14 ~ 7.06 (m, 15H Ph$_3$CMe), 6.87 (d, J_{HH} = 6.69 Hz, 2H free *p*-toluidine), 6.86 (d,

overlap with free *p*-toluidine 4H *p*-tolyl), 6.76 (d, J = 6.42 Hz, 4H *p*-tolylN), 6.41 (d, J = 6.42 Hz, 2H free *p*-toluidine) 5.69 (s, 5H Cp), 3.75 (broad, NH *p*-toluidine), 2.17 (s broad, 6H, CH_3 *p*-tolylN), 2.13 (s, 3H CH_3 free *p*-toluidine), 2.11 (s broad, 6H, CH_3 *p*-tolylN), 2.04 (s, 3H CH_3, Ph_3CMe). ^{13}C {^1H}NMR (125 MHz, C_6D_5Br, -25 ºC): δ 148.89 (*ipso*-C Ph_3CMe), 145.52 (*ipso*-C *p*-tolylN), 148.55 (d, J_{CF} = 241.19 Hz, *o*-CF $B(C_6F_5)_4$), 143.79 (*ipso*-C *p*-tolylN), 143.63 (*ipso*-C, *p*-toluidine), 138.07 (dd, J_{CF} = 242.97 Hz, J_{CF} = 233.75 Hz, *p*-CF , *m*-CF $B(C_6F_5)_4$), 131.19 (CH *p*-tolylN, overlap with the solvent), 129.74 (CH, *p*-toluidine), 129.63 (CH *p*-tolyl, overlap with the solvent), 128.77 (CH *p*-tolylN), 128.68 (CH Ph_3CMe), 127.80 (*ipso*-C, *p*-toluidine), 127.74 (CH Ph_3CMe), 127.23 (*ipso*-C *p*-tolylN), 126.59 (*ipso*-C *p*-tolylN), 126.47 (CH, *p*-tolylN overlap with the solvent), 125.87 (CH, Ph_3CMe), 125.05 (br, *ipso*-C $B(C_6F_5)_4$), 116.35 (CH *p*-tolylN), 115.24 (CH, *p*-toluidine), 110.14 (CH Cp), 52.47 (*C*, Ph_3CMe) , 30.49 (CH_3, Ph_3CMe) , 21.57 (br, CH_3, *p*-tolylN), 20.50 (CH_3, *p*-toluidine), 20.38 (CH_3, *p*-tolylN). ^{19}F {^1H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ – 132.14 (s, *o*-F, $B(C_6F_5)_4$), - 162.33 (t, J = 20.26 Hz, *p*-F, $B(C_6F_5)_4$), -166.25 (br, m-F, $B(C_6F_5)_4$). ^{51}V NMR (131 MHz, C_6D_5Br, 25 °C, $VOCl_3$ external standard): δ -554.33 (broad).

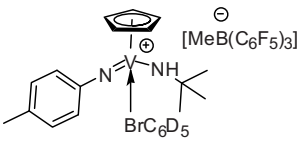
Generation of [Cp(*p*-tolylNH)V(N-*p*-tolyl)(*p*-tolylNH$_2$)][MeB(C$_6$F$_5$)$_3$] (4.3)



To a freshly generated solution of **2.14**[32] (0.06 mmol) in 0.6 mL of C_6D_5Br, 0.59 mmol of *p*-toluidine was added. ^1H NMR spectroscopy showed full conversion to **4.3** within 1h, affording a red-purple solution. ^1H and ^{13}C NMR of the cation are similar to **4.2**. ^1H NMR (400 MHz, C_6D_5Br, 25 °C): δ 12.77 (s broad, 1H, NH), 6.86 (d, 4H *p*-tolyl overlap with free *p*-toluidine), 6.79 (d, J = 7.02 Hz, 4H *p*-tolyl), 5.74 (s, 5H Cp), 2.17 (s, 3H CH_3 *p*-tolylN), 2.14 (s, 3H CH_3 *p*-tolylN), 1.16 (s broad, 3H B-Me). ^{13}C {^1H}NMR (125 MHz, C_6D_5Br, -25 ºC): δ 148.70 (d, J_{CF} = 248.3 Hz, *o*-CF $B(C_6F_5)_3$), 147.86 (d, J_{CF} = 239.6 Hz, *p*-CF $B(C_6F_5)_3$), 136.62 (d, J_{CF} = 244.4 Hz, *m*-CF $B(C_6F_5)_3$), 127.50 (CH, *p*-tolylN), 126.47 (CH, *p*-tolyl overlap with the solvent), 121.34 (*C*H, *p*-tolylN), 110.10 (*C*H Cp), 20.74 (br, CH_3, *p*-tolylN), 20.51 (CH_3, *p*-tolylN), 11.20 (br, B-Me). ^{19}F {^1H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ –

132.29 (d, J = 21.80 Hz *o*-F, B(C_6F_5)$_3$), -133.03* (s, *o*-F), -156.32* (t, J = 20.28 Hz, *p*-F, B(C_6F_5)$_3$), -162.77* (t, J = 19.51, Hz, *m*-F, B(C_6F_5)$_3$), - 163.89 (t, J = 20.50 Hz, *p*-F, B(C_6F_5)$_3$), -166.53 (t, J = 19.56, Hz, *m*-F, B(C_6F_5)$_3$). Resonances marked with an asterisk are from the contact ion-pair (20%).

Generation of [Cp(*t*-BuNH)V(N-*p*-tolyl)(*t*-BuNH$_2$)][MeB(C_6F_5)$_3$] (4.4)



To a freshly generated solution of **2.14**[32] (0.05 mmol) in 0.6 mL C_6D_5Br, 0.50 mmol of *t*-BuNH$_2$ was added. ^{1}H NMR spectroscopy showed full conversion to [Cp(*t*-BuNH)V(N-*p*-tolyl)(*t*-BuNH$_2$)][MeB(C_6F_5)$_3$] within 0.5 h at 80 ºC. ^{1}H NMR (400 MHz, C_6D_5Br , 25 ºC): δ 12.30 (s broad, 1H, NH), 6.85 (d, J_{HH} = 6.5 Hz, 2H, *p*-tolylN), 6.50 (d, J = 6.42 Hz, 2H *p*-tolylN), 5.78 (s, 5H Cp), 2.18 (s, 3H CH_3 *p*-tolylN), 1.17 (s, 9H CH_3, *t*-BuNH), 1.00 ([MeB(C_6F_5)$_3$] overlap with free *t*-BuNH$_2$). ^{13}C {^{1}H}NMR (125 MHz, C_6D_5Br, 25 ºC): δ 148.75 (d, J_{CF} = 240.5 Hz, *o*-CF B(C_6F_5)$_3$), 137.91 (d, J_{CF} = 131.5 Hz, *p*-CF B(C_6F_5)$_3$), 136.27 (d, J_{CF} = 137.4 Hz, *m*-CF B(C_6F_5)$_3$), 131.23 (CH *p*-tolylN), 129.67 (CH *p*-tolylN), 108.5 (CH Cp), 32.53 (CH$_3$, free *t*-BuNH$_2$), 30.81 (CH$_3$, *p*-tolylN), B-Me was not observed. ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 ºC): δ – 131.85 (d, J = 19.88 Hz *o*-F, B(C_6F_5)$_3$), -132.0* (s, *o*-F B(C_6F_5)$_3$), -155.77* (t, J = 20.88 Hz, *p*-F, B(C_6F_5)$_3$), -162.22* (t, J = 18.94, Hz, *m*-F, B(C_6F_5)$_3$), -163.85 (t, J = 20.78 Hz, *p*-F, B(C_6F_5)$_3$), -166.36 (t, J = 20.34, Hz, *m*-F, B(C_6F_5)$_3$). Resonances marked with an asterisk are from the contact ion-pair (19%). ^{51}V NMR (131 MHz, C_6D_5Br, 25 °C, $VOCl_3$ external standard): δ -692.82 (br).

Free *p*-tolylNH$_2$: ^{1}H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 6.86 (d, J = 7.83 Hz, 2H CH *p*-tolylN), 6.43 (d, J = 8.33 Hz, 2H CH *p*-tolylN), 3.22 (br, 1H NH), 2.14 (s, 3H CH_3 *p*-tolylN).

Catalytic hydroamination of alkynes with *p*-toluidine using cationic vanadium complexes 4.2 and 4.3.

All hydroamination experiments were performed on NMR scale in NMR tubes with a Teflon (Young) valve. To a freshly prepared solution of **2.6**[32] (0.045 g, 0.045 mmol) in 0.6 mL C_6D_5Br, 10 equivalents of *p*-toluidine (0.048 g, 0.45 mmol)

were added. This was allowed to stand for 1 h at ambient temperature (to generate the vanadium complex **4.2**). Subsequently, 10 equivalents of alkyne (*i.e* PhCCH 0.046 g, 0.45 mmol) and cyclooctane or cyclohexane (0.09 mmol) were added to the reaction mixture. The tube was placed at 80 ºC and monitored by ^{1}H NMR spectroscopy. Apart from the ^{1}H NMR spectroscopy, the reaction mixtures were analyzed by GC-MS and GC as well. The same procedure was used when **4.3** was employed.

Catalytic hydroamination of PhCCH with *t*-BuNH$_2$ using 4.4.

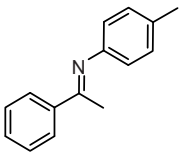
10 equivalents of *t*-BuNH$_2$ (0.033 g, 0.45 mmol) were added to a freshly generated cationic species **2.14**[32] (0.038, 0.045 mmol) in 0.6 mL of C_6D_5Br. The NMR tube was placed at 80 ºC for 0.5 h, generating **4.4**. Afterwards, 10 equivalents of PhCCH (0.046 g, 0.45 mmol) were added and the reaction mixture was placed at 80 ºC till full conversion of the PhCCH. Cp_2Fe (0.045 mmol) was used as internal standard. The reaction was monitored by ^{1}H NMR spectroscopy and analyzed by GC-MS and GC as well.

Catalytic hydroamination of terminal alkyne with *t*-BuNH$_2$ using the neutral vanadium complex 2.7 as catalyst.

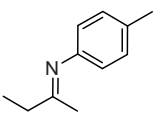
All hydroamination experiments were performed in NMR tubes with a Teflon (Young) valve. To a solution of **2.7** (0.01 g, 0.037 mmol) in benzene-d_6 (0.6 mL), 10 equiv of *t*-BuNH$_2$ (0.03g, 0.37 mmol) and 10 equiv of alkyne (*i.e.* PhCCH 0.038 g, 0.37 mmol) were added. The reaction mixture was monitored by ^{1}H NMR spectroscopy and kept at 80 ºC to full conversion of the alkyne. GC-MS and GC analyses were performed as well.

The same procedure was used also for the hydroamination reactions with the neutral vanadium complexes **2.2**, **2.3** and **2.9**.

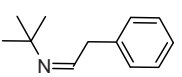
Hydroamination products



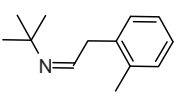
Phenyl ethyl ketone (3.0 mmol) and *p*-toluidine (3.1 mmol) were dissolved in Ether (5 mL) containing 4 Å mol sieves (6 g) at room temperature. Stirring was continued for 15 h and the mol sieves were filtered off. Removal of solvent *in vacuo* gave the imine as a yellow oil in a quantitative yield with trace amounts of *p*-toluidine present (^{1}H NMR analysis). The imine was used without further purification. Spectroscopic data were in accordance with those reported in literature.[31]



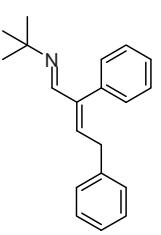
2 butanone (10 mmol 0.6 ml) and *p*-toluidine (10 mmol 1.07g) were dissolved in Ether (10 ml) containing 4 Å mol sieves (12 g). The mixture was stirred at room temperature for 15 h after which the mol sieves were filtered off. Removing the solvent *in vacuo* gave the imine as a yellow oil in a quantitative yield with trace amounts of *p*-toluidine present. The imine was used without further purification. Spectroscopic data were in accordance with those reported in literature. [31]



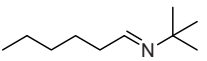
NMR data for the hydroamination product: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.49 (t, J = 4.26 Hz 1H CH(C=N)), 7.21 ~ 7.10 (m, 5H overlap with solvent), 3.46 (d, J = 4.52 Hz 2H CH_2), 1.11 (s, 9H CH_3 *t*-Bu).



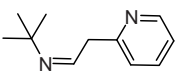
NMR data for the hydroamination product: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.43 (t, J = 4.60 Hz 1H CH(C=N)), 7.12 ~ 7.02 (m, 4H CH Ph), 3.46 (d, J = 4.66 Hz 2H CH_2), 2.16 (s, 3H CH_3 Ph), 1.09 (s, 9H CH_3 *t*-Bu).



NMR data for compound **h** from the hydroamination mixture of the PhCCH with *t*-BuNH_2 reaction in the presence of neutral vanadium complex **2.7**: ^{1}H NMR (400 MHz, C_6D_5Br, 25 °C): δ 7.55 ~ 6.94 (m, CH 10H Ph overlap with solvent), 6.74 (t, J = 11.86 Hz 1H CH), 5.40 (d, J = 12.7 Hz 1H CH), 3.47 (d, J = 9.46 Hz 2H CH_2), 0.90 (s, 9H CH_3 *t*-Bu). GC-MS: *m/z* 277, 262, 231, 220, 202, 115, 102.

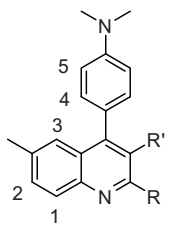


NMR data of the hydroamination product of 1-hexyne and *t*-$BuNH_2$ using **2.7**as catalyst. Spectroscopic data were in accordance with those reported in literature.[33] ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.45 (t, *J* = 4.30 Hz 1H CH(C=N)), 2.13 (dt, *J* = 7.43, 7.38, 4.80 Hz, 2H CH_2), 1.44 (m, 2H CH_2), 1.15 (s, 9H CH_3 *t*-Bu), 0.83 (t, *J* = 6.58 Hz, 3H CH_3).



NMR data for the hydroamination product: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 9.71 (d, *J* = 9.85 Hz, 1H CH), 8.94 (br, 1H CH), 7.68 (br, 1H CH (C=N)), 6.59 ~ 6.02 (m, 2H CH), 4.72 (d, *J* = 7.89 Hz, 2H CH_2), 0.68 ((s, 9H CH_3 *t*-Bu).

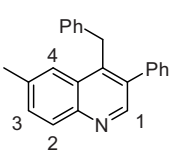
Catalytic carboamination of phenylacetylene and aldimine using 4.2 as catalyst. [34]



R = Ph, R' = H (**f**)
R = H, R' = Ph (**g**)

To a solution of **2.6** (ca. 0.027 mmol) in C_6D_5Br (0.6 mL) prepared in an NMR tube (equipped with a Teflon Young valve) as described in Chapter 2, 10 equivalents of aldimine (0.064 g, 0.27 mmol) was added. Subsequently, 10 equivalents of PhCCH (0.027 g, 0.27 mmol) was added to the reaction mixture. The tube was placed at 80 ºC and monitored by ^{1}H NMR spectroscopy for 7days. Apart from the ^{1}H NMR spectroscopy, the reaction mixtures were analyzed by GC-MS as well. ^{1}H NMR (400 MHz, C_6D_5Br, 25 ºC), isomer **g**: δ 8.31 (s, 1H N=CH), 7.31 (d, *J* = 8.0 Hz, 1H CH, position 1), 7.17 (m, CH overlap positions 2- 3- 4), 7.11-6.96 (m, CH Ph), 6.25 (d, *J* = 8.4 Hz, 2H CH, position 5), 2.53 (s, 6H CH_3), 2.18 (s, 3H CH_3). Isomer **f**: δ 7.85 (d, *J* = 6.37 Hz, 2H Ph), 7.41 (d, *J* = 7.2 Hz, 1H CH, position 1), 7.11-6.96 (m, CH Ph, overlap positions 2-3-4, CH-R'), 6.43 (m, CH, position 5), 2.56 (s, 6H CH_3), 2.17 (s, 3H CH_3). GC-MS: *m/z* 338, 321, 294, 278, 207, 169, 161, 134, 121.

Characterization of substituted quinoline (**b**).



The substituted quinoline **b** formed during the hydroamination reaction of PhCCH and *p*-toluidine in the presence of vanadium catalyst **4.2** was isolated from the reaction mixture by column chromatograph over silica, followed by preparative HPLC and

preparative GC. The product was analyzed by NMR spectroscopy, GC-MS, EI^+, CI^+ and ES^+. In the GC-Ms spectrum compound **b** shows a strong M – 1 (base) peak, usually encountered for cyclic amine/imine[35] (*m/z* M = 309, M-1= 308, 293, 230, 154, 146); LRMS (EI): *m/z* M – 1: 308.1483 (100%), M: 309.1530 (58%), M + 1: 310.1590 (18 %); CI: m/z 310 (100 %), 311 (31 %), 312 (5.4 %); ES: 310. ^{1}H NMR (400 MHz, CD_3Cl, 25 ºC): δ 9.10 (d, *J* = 9.12 Hz, 1H N=CH position 1), 8.40 (s, 1H CH, position 4), 7.86 (d, *J* = 8.71 Hz, 1H CH, position 2), 7.74 (s, 1H), 7.51 (m, 2H Ph), 7.19 (d, *J* = 7.15 Hz, 2H), 7.09 (m, 4H), 6.94 (m, 2H), 4.90 (s, 2H CH_2), 2.63 (s, 3H CH_3). ^{13}C {^{1}H} NMR (125 MHz, CD_3Cl, 25 ºC): δ 144.07 (CH N=CH, 1), 136.43, 129.43, 129.33, 129.28, 129.07, 128.61, 127.23, 126.39 (CH, 4), 37.32 (CH_2), 28.10 (CH_3), quaternary carbons were not observed.

4.6 References

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[18] NMR data for free *i*-Pr_2NH: ^1H NMR (400 MHz, THF-d_8 25 ºC): δ 2.86 (sept, J_{HH} = 6.3 Hz, 2H CH *i*-Pr_2N), 0.96 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), 0.30 (s broad, 1H NH). NMR data for free *i*-Pr_2NH: ^1H NMR (400 MHz, C_6D_5Br, 25 ºC): δ 2.80 (sept, J_{HH} = 6.2 Hz, 2H CH *i*-Pr_2N), 0.95 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), 0.44 (s broad, 1H NH).

[19] The starting material, **2.5**, was crystallized from non-deuterated THF.

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[21] CG-MS analysis showed for 1-hexyne hydroamination reaction the presence of compounds with Mw = 271 (two isomers t_R = 14.3 and 14.5 min), Mw = 283 (t_R = 15.9 min) also.

[22] Apart from the cyclotrimers, dimer and tetramer products of phenylacetylene other unknown side products, which probably consume phenylacetylene are observed also: Mw = 211 (t_R =13.51 min), Mw = 219 (t_R = 15.62 min), Mw = 299, Mw = 313 (t_R = 18.63 min).

[23] GC-MS analysis displays the presence of undetermined compounds with mass of Mw = 358 (t_R = 19.4 min).

[24] In the reaction mixtures of entry 2 and 3 were formed ca. 6 % phenylacetylene dimer, 8 % phenylacetylene tetramer, < 4 % pentamer (Mw = 514) together with traces of undetermined product with mass of Mw = 322, t_R = 18.2 min.

[25] Products as a result of PhCCH protonation (*e.g* styrene, ethyl benzene) were not observed.

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Chapter 5

Vanadium(V) amido-imido complexes with *ansa* Cp-arene ligands

Vanadium(V) imido-amido complexes with a cyclopentadienyl ligand bearing a pendant arene group were prepared. Generation of cationic vanadium species from neutral precursors resulted in ansa-η^5,η^1-coordination of the Cp-arene ligand, in which the pendant arene is η^1-coordinated to the metal via the ortho CH carbon, thus stabilizing the electronically unsaturated vanadium center. The strength of the vanadium – arene interaction was investigated by variable-temperature and 2D NMR spectroscopy. Changing from C_1- to C_2-bridged ligands and from p-tolyl imido to the more electron donating t-Bu imido group decreases the strength of the metal – arene interaction.

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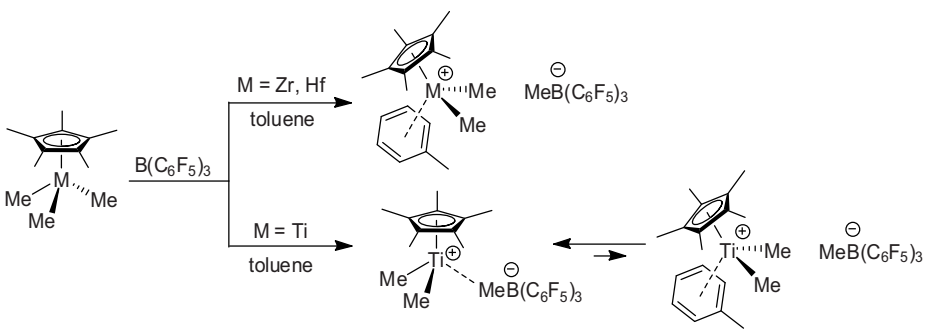
5.1 Introduction

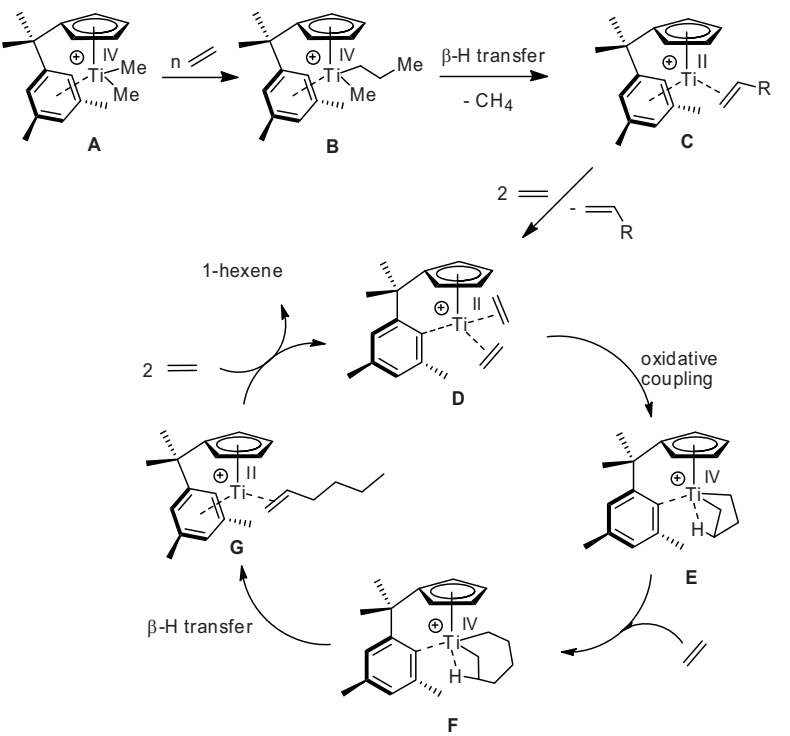
Hemilabile ligands[1] (*i.e.* multidentate ligands that contain both tightly bound and loosely/reversibly bound moieties) are receiving increasing attention[2,3,4,5,7,8,9] in catalysis due to the fact that they can stabilize metal centers (chelate effect), but keep the metal accessible for substrate molecules. In previous chapters it was shown that electronically unsaturated Cp-imido vanadium species can be generated in two ways: the cationic CpV(V)-imido-amido species by methyl abstraction from Cp(*i*-Pr_2N)V(NR)Me (R = *p*-tolyl, *t*-Bu) (Chapter 2) and the neutral CpV(III)-imido fragment by thermolysis of Cp(*i*-Pr_2N)V(NR)Me (R = *p*-tolyl, *t*-Bu) complexes (Chapter 3). It was also observed that stabilization of the cationic species by coordination of THF quenches its activity for catalytic hydroamination. Thus, transient stabilization of the cationic species by a more weakly bound ligand could be favorable for reactivity. Baird *et al*. reported that arenes can function as labile ligands binding reversibly to $[(\eta^5\text{-}C_5Me_5)MMe_2]^+$ cations (M = Ti, Zr, Hf). The metal-arene interaction was found to be significantly weaker for Ti than for Zr and Hf (Scheme 1).[6]



Scheme 1

This work stimulated investigations into the ability of phenyl groups to act as weakly bound moieties in hemilabile ancillary ligands, *e.g* the phenyl moiety attached as pendant to the cyclopentadienyl group. Thus it was observed that cationic $[CpTiMe_2]^+$ can be stabilized by a pendant arene group on the cyclopentadienyl ligand.[7,8] In addition to the stabilizing ability of pendant arene groups, they can also modify the reactivity of the metal centre. In the case of the cationic Ti species, a pendant arene group transformed it from an ethylene polymerization catalyst to a highly selective ethylene trimerization catalyst.[9,10]

Computational studies[11] suggest that in this system the pendant arene adopts various bonding modes through the catalytic cycle (mechanism shown in Scheme 2): (a) η^6 on Ti(IV) dialkyl species (**A**); (b) η^1 on Ti(II) bis(ethene) adducts (**D**) and Ti(IV) β-agostic species (**E**, **F**); (c) η^6 with a partially reduced arene on Ti(II) mono(alkene) adducts (**G**). Of the calculated coordination modes of arene, the two different η^6 modes ((a) and (c)) have been demonstrated by crystal structures.[12,13] As cationic $[Cp(NR'_2)V(NR)]^+$ complexes are more electron-rich than the cationic $[Cp^RTiMe_2]^+$ complex, they may provide an opportunity to observe the η^1-bonding mode in an *ansa*-Cp-arene complexes. Furthermore, a pendant arene group may help to stabilize the unsaturated V(III) species "CpV(NR)" that (as seen in Chapter 3) are generated during the thermolysis of *ansa*-Cp(*i*-Pr_2N)V(NR)Me (R = *p*-tolyl, *t*-Bu) complexes.

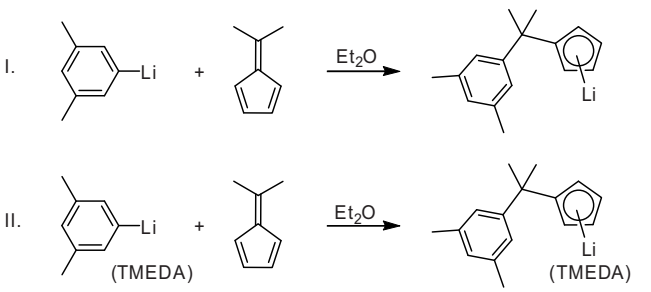


Scheme 2

In this chapter the synthesis and chemistry of Cp vanadium imido-amido compounds with arene functionalized cyclopentadienyl ligands and their cationic vanadium(V) derivatives is described.

5.2 Neutral vanadium(V) amido-imido *ansa*-Cp-arene complexes

Aryl-cyclopentadienyl ligands with $–CMe_2Ar$ and $–CMe_2CH_2Ar$ (Ar = 3,5-dimethylphenyl) substituents can be prepared easily from the reaction of the 6,6-dimethylfulvene[14] with the appropriate aryllithium salts (Scheme 3).[9a,12] The 3,5-(dimethyl)-phenyl group was chosen initially to provide a stronger donor interaction and make arene cyclometallation[15] less favorable.

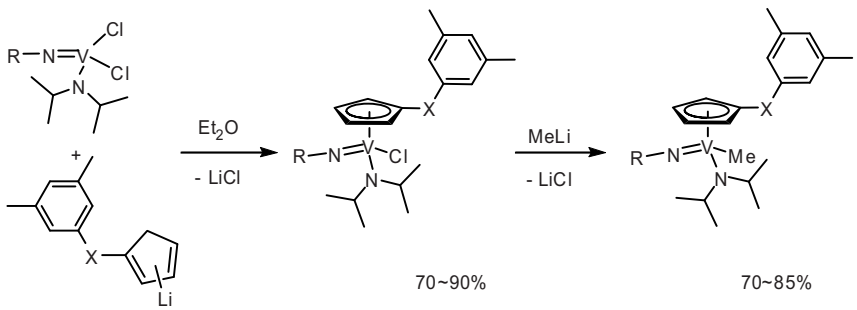


Scheme 3

Pendant arene-cyclopentadienyl vanadium amido-imido monochlorides are readily prepared via metathesis of the appropriate cyclopentadienyllithium reagents with vanadium imido-amido dichlorides [(*i*-Pr_2N)V(NR)Cl_2] (R = *p*-tolyl, *t*-Bu) generating: (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**5.1**), (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**5.2**), (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Cl (**5.3**), (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Cl (**5.4**) (Scheme 4). Compounds **5.1**, **5.3** and **5.4** are red solids, whereas **5.2** was obtained as a red oil. Recrystallization from pentane afforded crystals of **5.1** and **5.4** suitable for single crystal X-ray diffraction. Their structures are shown in Figure 1 (**5.1**) and Figure 2 (**5.4**) with selected bond lengths and angles in Table 1 (**5.1**) and Table 2 (**5.4**).

Methylation of compounds **5.1**, **5.2**, **5.3** and **5.4** with MeLi in diethylether at low temperatures (-40 º ~ -10 ºC) afforded in good yields the methyl derivatives (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.5**), (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.6**), (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-

t-Bu)Me (**5.7**) and (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.8**) (Scheme 4).



Scheme 4

Crystallization from pentane (-30 ºC) gave compound **5.5** as red crystals, **5.6** as a red-brown foam, **5.7** as a green-yellow solid and compound **5.8** was isolated as a green-brown oil. The vanadium methyl compounds **5.5**, **5.6**, **5.7** and **5.8** were fully characterized by NMR spectroscopy. Moreover, **5.5** was analyzed by X-ray diffraction as well, and the molecular structure is depicted in Figure 1 with the selected bond lengths and angles presented in Table 1.

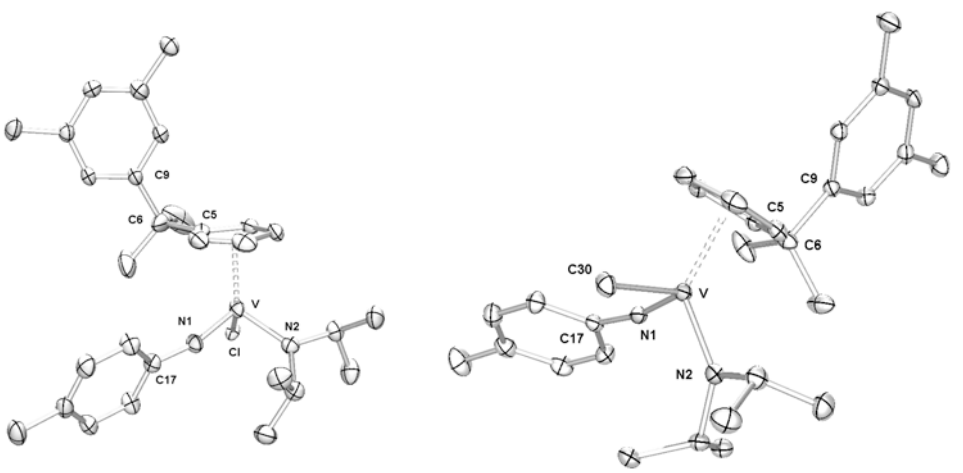


Figure 1. *Molecular structure of **5.1** (left) and **5.5** (right) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.*

Table 1. *The selected bond lengths (Å) and angles (°) of compounds **5.1** and **5.5**.*

Bond lengths (Å)	**5.1**	**5.5**
V – N1	1.658(3)	1.6683(19)
V – N2	1.851(3)	1.8735(18)
V – Cg*	1.688	1.691
V – R	2.3462(12)	2.120(2)
Bond angles (°)		
V – N 1 – C17	166.9(3)	167.06(15)
N1 – V – N2	100.80(16)	103.60(8)
N1 – V – R	101.41(13)	93.55(8)
N2 – V – R	97.61(12)	95.89(9)
C5 – C6 – C9	101.6(4)	110.06(16)

*Cg is the centroid of the C(1) - C(5) ring, R = Cl (**5.1**); R = Me (**5.5**).

The structures presented in Figure 1 and 2 show the familiar three-legged piano-stool geometry. The arene substituents adopt a conformation roughly perpendicular to the plane of the cyclopentadienyl ring, and there is no indication of any type of interaction between the aryl ring and the metal centre. ^{1}H NMR spectroscopy shows one singlet resonance for the *o*-CH protons of the non-coordinated arene (δ 6.96 ppm **5.5**, 6.39 ppm **5.6**, 7.03 ppm **5.7** and 6.57 ppm **5.8**). Similarly, the Ar-*Me* group shows a sharp singlet ^{1}H NMR resonance (δ 2.11 ppm **5.5**, δ 2.20 ppm **5.6**, δ 2.17 ppm **5.7** and δ 2.21 ppm **5.8**). These compounds display an asymmetric configuration around the metal center in solution indicated by the four distinct absorptions due to the cyclopentadienyl ligand resonances. For the compounds with an extra CH_2- group in the bridge (**5.6** and **5.8**), this is indicated by the diastereotopic benzyl methylene protons.

The methyl vanadium complexes **5.5**, **5.6**, **5.7** and **5.8** are thermally labile with compound **5.7** being the most unstable (decomposing at ambient temperature in C_6D_6 solution within 10 h). The thermolysis of compounds **5.5**, **5.6**, **5.7** and **5.8** is discussed in Section 5.3.

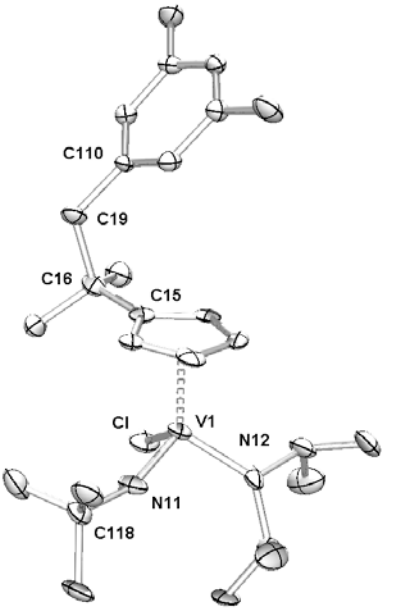


Figure 2 *Molecular structure of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(i-Pr_2N)V(N-t-Bu)Cl (**5.4**) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.*

Table 2. *The selected bond lengths (Å) and angles (°) of compound **5.4**.*

Bond lengths	(Å)		
V1 – N11	1.654(6)	V1 – Cg(1)*	1.701
V1 – N12	1.854(6)	V1 – Cl1	2.323(3)
Bond angles	**(°)**		
V1 – N11 – C118	160.1(6)	C15 – C16 – C19	107.1(8)
C16 – C19 – C110	116.2(7)		

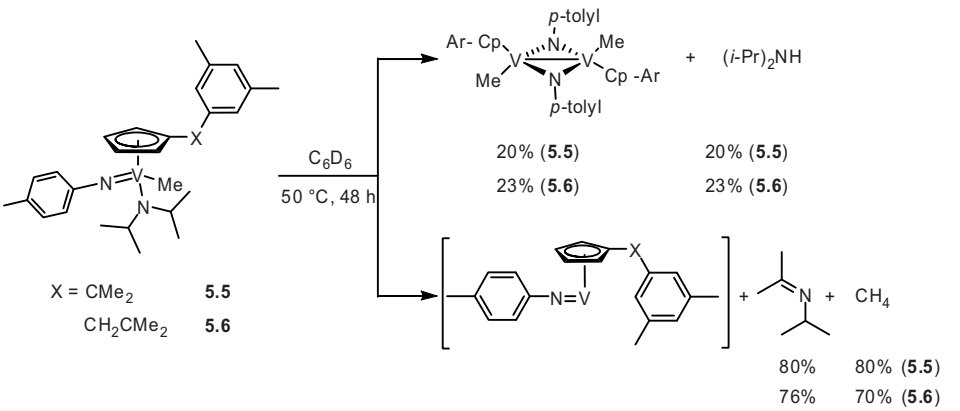
*Cg is the centroid of the C(1) - C(5) ring.

5.3 Thermolysis of Cp-arene vanadium amido imido methyl complexes

5.3.1 Thermal stability of vanadium(V) complexes with a Cp-arene ancillary ligand

Previously it was shown (Chapter 3) that low valent vanadium species can be generated by thermal decomposition of the vanadium(V) compounds Cp(*i*-Pr_2N)V(N-*t*-Bu)Me (**2.2**) and Cp(*i*-Pr_2N)V(N-*p*-tolyl)Me (**2.3**). In this section the thermal stability of vanadium(V) complexes with a pendant arene group, which might help to stabilize the unsaturated V(III) species "CpV(NR)", was investigated.

Thermolysis of (Ar-CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*p*-tolyl)Me (Ar = 3,5-$Me_2C_6H_3$) (**5.5**) at 50 ºC in benzene-d_6 was monitored by ^{1}H NMR spectroscopy over 48 h after which the starting material was fully converted. The ^{1}H NMR spectrum shows methane liberation, together with formation of *N*-isopropyl-2-propanimine, diisopropyl amine and the dimeric vanadium(IV) complex [(Ar-CMe_2-η^5-C_5H_4)VMe(N-*p*-tolyl)]$_2$ (see data in experimental section). In Chapter 3 it was reported that thermolysis of **2.3** leads to the formation of a similar vanadium dimer, [CpV(μ-N-*p*-tolyl)Me]$_2$ (**3.1**). It is evident that the radical decomposition pathway leading to the V(IV) dimer is not prevented by introduction of a substituted cyclopentadienyl group. As in the thermolysis of **2.2** and **2.3**, ^{2}H-NMR spectroscopy does not show the presence of *i*-Pr_2ND hence the solvent can be excluded as the hydrogen source for the diisopropyl amine formation. In addition, the ^{1}H NMR spectrum of the mixture shows broad resonances over a wide range (from δ 46.82 to -25.84 ppm, see exp. section). From the gas (measured by Toepler pump) and organic products balance (Cp_2Fe as internal standard) it can be concluded that 80% of the vanadium(V) complex is converted to a vanadium (III)-imido species and 20% to the vanadium(IV) imido bridged dimer (Scheme 5). The acquired spectral data do not provide clear information on possible stabilization of the V(III) species by the arene moiety for the C_1 bridged vanadium compound.



Scheme 5

As the "CpV(III)-imido" species has a 14 v.e. count (provided the lone pair of the imido group is involved, which it usually is), stabilization of this species by the pendant arene is likely to occur by a mode that does not involve all of the arene carbons. Such a partial coordination can be affected by differences in flexibility of the Cp-arene bridge. Thus (Ar-CH_2CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.6**), which has an extra -CH_2 in the bridge, was similarly decomposed thermally at 50 ºC in two different solvents, C_6D_6 and THF-d_8. The thermolysis gave a similar result in both solvents. In comparison with the thermolysis of **5.5**, the ^{1}H NMR spectrum of the **5.6** thermolysis mixture exhibits quite a different pattern. ^{1}H NMR spectroscopic data show formation of methane, *N*-isopropyl-2-propanimine, diisopropyl amine and the vanadium(IV) imido bridged dimer [(η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)V(N-*p*-tolyl)Me]$_2$ as well (Scheme 4; for data see experimental section). As for **5.5**, the diisopropylamine is not deuterated when the reaction is performed in deuterated solvent. The remaining ^{1}H NMR resonances in the mixture (which may derive from the V(III) species) do not show as broad a chemical shift range as that observed for the thermolysis of **5.5** (in the thermolysis of **5.6**: δ 8.87 ($\Delta\nu_{1/2}$ = 49 Hz), 4.71 ($\Delta\nu_{1/2}$ = 45 Hz)). This suggests that different type of compound is formed. EPR analysis of the thermolysis mixture revealed the presence of a typical octet hyperfine structure (^{51}V, I = 7/2, 99.8% natural abundance) in benzene solution at 298 K (Figure 3) with g = 1.92 and a (^{51}V) ~ 27G.

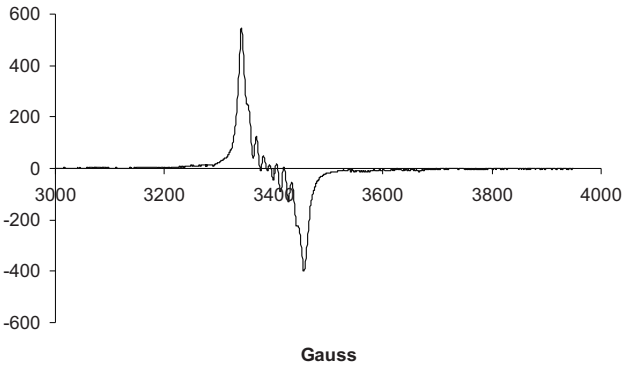
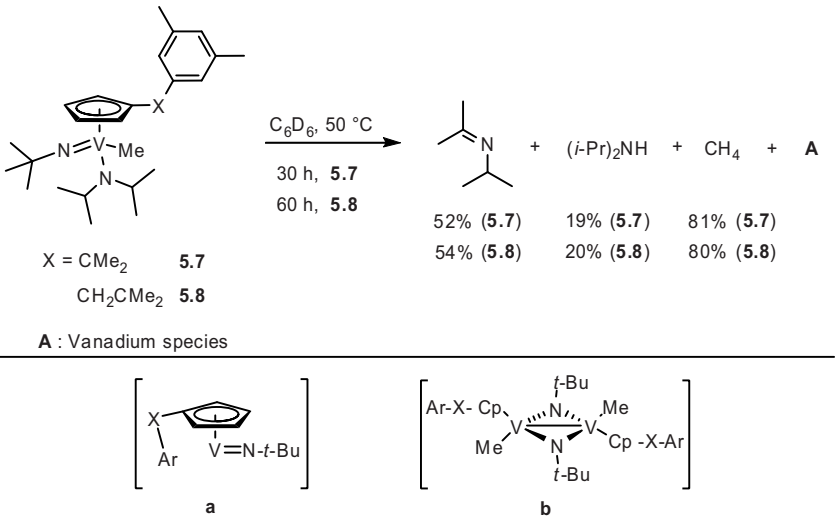


Figure 3. *EPR spectrum of the thermolysis mixture of compound* ***5.6*** *in benzene at 298K.*

The presence of an EPR signal suggests the formation of a monomeric vanadium (IV) d^1 species, possibly kept monomeric by arene coordination. Nevertheless, the exact nature and the amount of this vanadium(IV) d^1 species remains unclear so far.

Further thermolysis reactions were carried out with the (Ar-CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.7**) and (Ar-CH_2CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.8**) (Ar =3,5-$Me_2C_6H_3$) systems in C_6D_6 at 50 ºC for 30 h and 60 h, respectively (Scheme 7). The ^{1}H NMR spectroscopic analysis of **5.7** and **5.8** thermolysis mixtures confirmed the presence of both *N*-isopropyl-2-propanimine and diisopropylamine (approximate ratio 2.7:1) in addition to liberation of methane (0.81 CH_4/V for **5.7** and 0.80 CH_4/V for **5.8** measured by Toepler pump). Again, the diisopropylamine is not deuterated (*vide supra*). The presence of diisopropylamine in the thermolysis mixture of the (Ar-X-Cp)(*i*-Pr_2N)V(N-*t*-Bu)Me (X = CMe_2, CH_2CMe_2) compounds is indicative for the generation of vanadium(IV) – methyl species (**b**, Scheme 6), as observed previously for the *p*-tolyl-imido vanadium complexes. The spectral data obtained from the **5.7** and **5.8** thermolysis mixtures, that can be assigned to dinuclear vanadium (IV)-methyl complex are: two absorptions in the cyclopentadienyl area, at δ 6.10 and δ 5.67 ppm for **5.7** and δ 5.48 and δ 6.04 ppm for **5.8**, together with an absorption for the V-CH_3 moiety (δ 0.27 ppm and δ -1.02 ppm respectively). Nevertheless, this is only the minor pathway in this decomposition (accounting for about 20% of the vanadium).



Scheme 6

Quantification of the organic products shows that liberation of methane accounts for the thermal decomposition of the other 80 % of the starting material. Nevertheless, only around 50 % *N*-isopropyl-2-propanimine is formed, suggesting that, in addition to the coupled methane and *N*-isopropyl-2-propanimine formation to yield the V(III)-imido species, a third decomposition pathway is present that liberates only methane or where the imine is coordinated to the unsaturated vanadium species. EPR investigation of the thermolysis mixture of **5.7** shows as a major species a well-defined signal (Figure 4) that can be attributed to a species with $S = 1/2$, probably a mononuclear V(IV) (d^1) species.[16] A typical octet hyperfine structure (^{51}V, I = 7/2, 99.8 % natural abundance) is present in solution (benzene at 298 K) with g = 1.91 and a (^{51}V) ~ 74 G. A possible hypothesis for the formation of such a vanadium(IV) species during the thermolysis could be that the monomeric form of the vanadium (IV)-methyl complex is in equilibrium with the dimeric form. DCl addition to the thermolysis mixture of complex **5.7** and GC-MS analysis of the organic components confirmed the presence of only the mono-deuterated ligand (C_5H_4D-CMe_2-3,5-$Me_2C_6H_3$, Mw = 213), suggesting that the arene is not *ortho*-metalated during the thermolysis process.

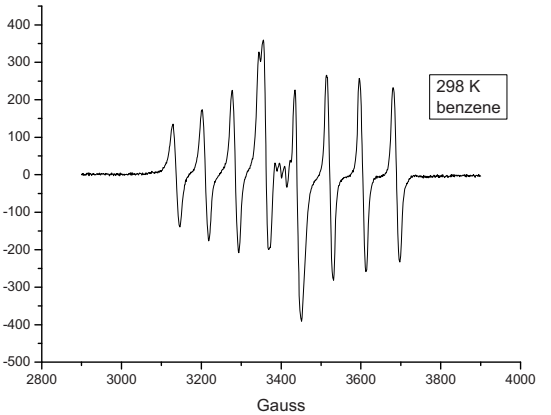


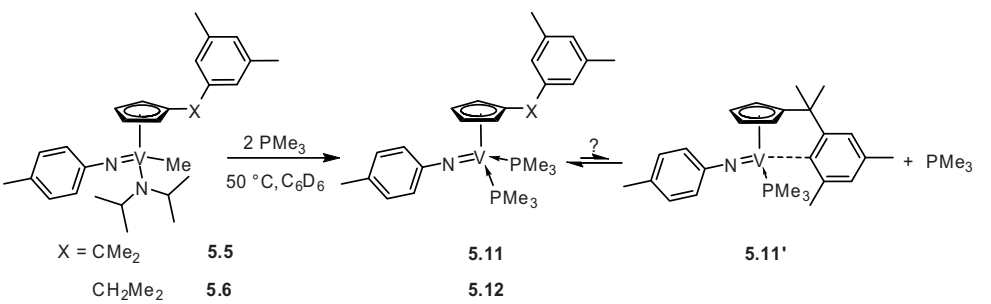
Figure 4. *EPR spectrum of the thermolysis mixture of compound* ***5.7*** *in benzene at 298 K.*

In contrast to the observations of the thermolysis mixture of the **5.7**, no EPR signal was observed for the thermolysis mixture of **5.8** (ambient temperature in benzene-d_6 solvent). This suggests two possibilities: a) generation of a diamagnetic 18 v.e. d^2 vanadium complex with the arene moiety coordinated in a η^4-fashion or b) generation of a $S = 1$ d^2 vanadium (III) species, both being EPR 'silent'. Unfortunately, low temperature ^{1}H NMR experiments in toluene did not provide conclusive evidence for a diamagnetic species with a coordinated arene group.

In addition to the ^{1}H NMR absorptions of the known organic products and the vanadium dimers, the ^{1}H NMR spectra of the **5.7** and **5.8** thermolysis mixtures showed, in the cyclopentadienyl area (δ 4.5-6.5 ppm), several resonances associated with diamagnetic species: 6 signals for the C_1-bridged complex and 4 signals for the C_2-bridged species, although at low intensities. Unfortunately, the aliphatic region is quite crowded precluding unambiguous assignment these species. After vacuum transfer of the volatiles, DCl was added to the remaining thermolysis mixture of complex **5.8** and GC-MS analysis of the organic components confirmed the presence of only the mono-deuterated ligand (C_5H_4D-CMe_2CH_2-3,5-$Me_2C_6H_3$, Mw = 227), suggesting that the arene is not *ortho*-metalated in the thermolysis process.

5.3.2 Vanadium(III) phosphine complexes with Cp-arene ligands

In Chapter 3 it was described that the thermolysis of V(V) imido amido methyl complexes in the presence of phosphines led to isolable vanadium(III)-imido phospine complexes. Here we extend this to the thermolysis of Cp-arene vanadium methyl complexes in the presence of phosphines (PMe_3 and dmpe) and try to see whether the pendant arene group is involved in any of these processes. Compound (Ar-CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*p*-tolyl)Me (Ar = 3,5-$Me_2C_6H_3$) (**5.5**) was thermolyzed in C_6D_6 in the presence of PMe_3 (1:2 ratio) over a period of 8 days at 50 ºC, after which the starting material was converted quantitatively into the complex (η^5-$C_5H_4CMe_2$-3,5-Me_2-C_6H_3)V(N-*p*-tolyl)(PMe_3)$_2$ (**5.11**, Scheme 7). The ^{51}V NMR spectrum shows a large downfield shift, from δ -556.48 ppm in the complex **5.5** to δ 265.96 ppm for **5.11**, comparable to that seen in Chapter 3 for the thermolysis of **2.3** in the presence of PMe_3. Nevertheless, the ^{1}H NMR spectrum of **5.11** shows line broadening for the cyclopentadienyl ligand and for the resonances of the *p*-tolylimido ligand. The ^{31}P NMR spectrum exhibits both a 'horned' plateau at δ 52.70 ($\Delta\nu_{top}$= 2659 Hz) – typical for phosphine coordinated to a vanadium center - as well as a broad resonance at δ - 61.4 ppm for free PMe_3. This, together with the observations made in the thermolysis of **5.7** in the presence of dmpe (*vide infra*) suggests the possibility that there is dynamic exchange involving the pendant arene group and one of the phosphines (Scheme 7, showing **5.11** and **5.11'**).



Scheme 7

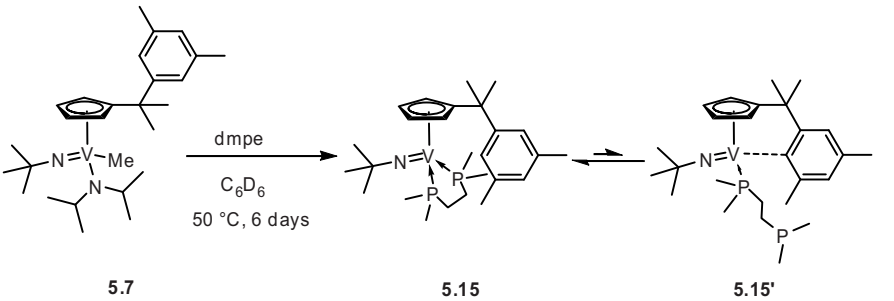
Thermolysis of the compound (Ar-CH_2CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.6**) in the presence of two equivalents of PMe_3 at 50 ºC for 6 days, provided the phosphine adduct (η^5-$C_5H_4CMe_2CH_2$-3,5-Me_2-C_6H_3)V(N-*p*-tolyl)(PMe_3)$_2$ (**5.12**, Scheme 8). The ^{1}H NMR resonances of **5.12** are sharp and the arene moiety shows

no evidence for interaction with the metal center. The ^{31}P NMR spectrum shows the typical 'horned' plateau (δ 52.5 ppm, $\Delta\nu_{top}$= 2564 Hz) indicating coordination of PMe_3 to vanadium, as well as a resonance at δ - 60.5 ppm for free PMe_3. If the specific spectral features of **5.11** described above are due to dynamics involving the pendant arene, this effect is absent in **5.12** where the spacer between the Cp and arene moieties is longer.

The thermolysis of **5.6** was also investigated in the presence of the chelating diphosphine ligand dmpe, generating the compound (Ar-CH_2CMe_2-η^5-C_5H_4)V(N-*p*-tolyl)(dmpe) (Ar = 3,5-$Me_2C_6H_3$) (**5.13**) in 97% yield (based on internal standard and methane measurements by Toepler pump 0.97 CH_4/V). When compared to the formation of **3.6**[17] under similar conditions, **5.12** and **5.13** are generated more selectively: no observable amount of V(IV) dimer was formed.

Thermolysis of the Cp-arene *t*-Bu-imido vanadium compounds **5.7** and **5.8** in the presence of phosphines results in the formation of the corresponding vanadium-phospine adducts. Hence, from (Ar-CH_2CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.8**) (Ar = 3,5-$Me_2C_6H_3$) in the presence of PMe_3 (1:2 ratio) the 18 v.e diamagnetic compound (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(PMe_3)$_2$ (**5.14**) was obtained after 6 days at 50 ºC. The ^{1}H NMR spectrum displays sharp absorptions for the newly formed complex and the coordination of PMe_3 to the vanadium center is indicated by the ^{31}P NMR spectrum with a typical plateau (δ 54.38 ppm, $\Delta\nu_{top}$= 2496).

Thermolysis of the C_1 bridged complex (Ar-CMe_2-η^5-C_5H_4)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.7**) (Ar = 3,5-$Me_2C_6H_3$) in the presence of the chelating diphosphine dmpe at 50 ºC for 6 days, yielded quantitative conversion of all the starting material into the complex (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(dmpe) (**5.15**). The two cyclopentadienyl absorptions of **5.15** exhibit line broadening, as do the resonances of the coordinated dmpe. This broadening again could suggest that in **5.15** the system 'shuttles' between (η^5-Cp-Ar)V(N-*t*-Bu)(κ^2-dmpe) and (η^5,η^1-Cp-Ar)V(N-*t*-Bu)(κ^1-dmpe) (Scheme 8). Similar phenomena are observed also for the compound (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(PMe_3)$_2$ (**5.22**), obtained from thermolysis of neutral vanadium-methyl complex **5.7** in the presence of two equivalents of PMe_3.

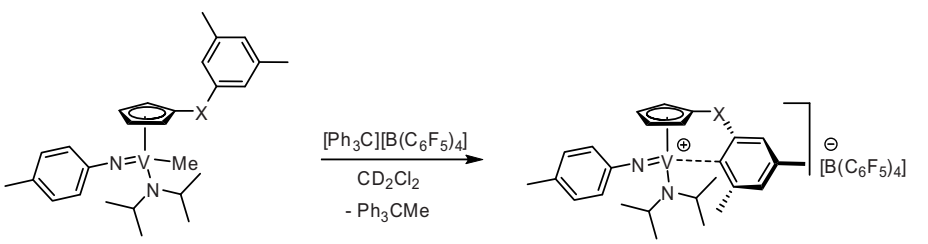


Scheme 8

It is likely on electronic grounds that any stabilizing interaction between the pendant arene group and the metal center in thesis systems will be limited to interaction with the arene *ortho* carbon. In that case this interaction will be most favorable for the ligand with the C_1 spacer, as such a chelating interaction benefits from geometric constraint.

5.4 Generation of cationic vanadium(V) complexes with *ansa*-Cp-arene ligands

Cationic vanadium (V) complexes can be generated from the corresponding neutral monomethyl derivatives using various reagents, as was shown in Chapters 2 and 4. Here the cationic *ansa*-Cp-arene vanadium(V) complexes generated by the methyl abstraction protocols using $[Ph_3C][B(C_6F_5)_4]$ is described. The neutral compound (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.5**) reacted with $[Ph_3C][B(C_6F_5)_4]$ in dichloromethane at ambient temperature to give quantitatively the first cationic vanadium(V) *ansa*-Cp-arene species **5.16** (Scheme 9).



Scheme 9

Crystallization from dichloromethane layered with cyclohexane gave crystals suitable for X-ray diffraction. The molecular structure of the cation of complex **5.16** is shown in Figure 4 and the crystallographic data are given in Table 3. The most notable feature of the cation [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(*p*-tolylN)]$^+$ (**5.16**), which has the *p*-tolyl-imido group slightly bent with V(1)-N(11)-C(117) = 157.85(15)°, is the bonding of the arene moiety of the *ansa*-Cp-arene ligand to vanadium center (Figure 5). One of the *ortho* carbon atoms shows a close approach to the metal center (V(1)-C(114) = 2.411(2) Å), whereas the other C(arene) atoms are much further away (Table 3), resulting in a complex with an *ansa*-(η^5-C_5H_4, η^1-arene) coordination mode.

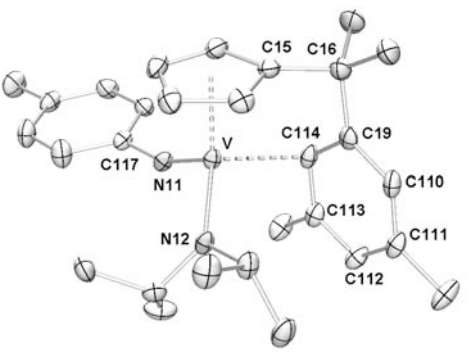


Figure 5. *Molecular structure of [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(i-Pr_2N)V(N-p-tolyl)][$B(C_6F_5)_4$] (**5.16**) showing 50% probability ellipsoids. Hydrogen atoms and the [$B(C_6F_5)_4$] anion are omitted for clarity.*

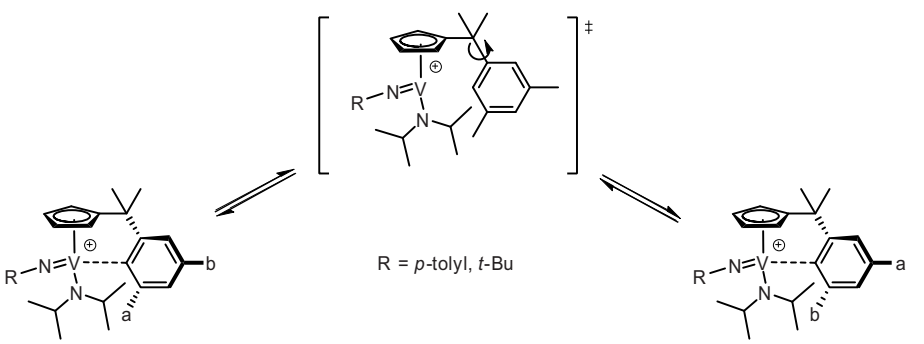
Table 3. *Selected bond distances (Å) and angles (°) of **5.16**.*

Bond lengths	(Å)		
V1 – N11	1.6774(17)	V1 – Cg(1)*	1.9674(11)
V1 – N12	1.8699(17)	V1 – Cg(2)#	3.1534(11)
V1 – C114	2.411(2)	V1 – C111	4.225(2)
V1 – C19	2.876(2)	V1 – C112	3.950(2)
V1 – C110	3.752(2)	V1 – C113	3.122(2)
Bond angles	(°)		
V1 – N11 – C117	157.85(15)	C15 – C16 – C19	102.76(17)
N11 – V1 – C114	99.99(8)		

*Cg is the centroid of the C(1) - C(5) ring. #Cg is the centroid of the C(19) - C(114) ring.

The C(15)-C(16)-C(19) angle of 102.76(17)° indicates that the ligand geometry for such an η^1-arene coordination is favorable and involves little strain[18]. The ring C-C bond lengths to the coordinated *o*-CH group (1.417(3) and 1.408(3) Å for C(19)-C(114) and C(113)-C(114), respectively) are longer than the remaining C-C bonds (av. 1.388 Å). The C-H bond of the coordinated *ortho* arene position deviates from the C6-plane by 9.7(16)°, as is observed for η^1-arene complexes of moderately strong Lewis acids (π/σ-intermediate bonding).[19] Similar η^1-arene binding of a pendant *p*-tolyl group to a cationic zirconium centre was recently inferred from spectroscopic and computational studies on the zirconocene cation [η^1-(4-Me-C_6H_4)-CMe_2-η^5-C_5H_4]$CpZr^+(CH_2Ph)$[20]. In that case, a ^{1}H NMR resonance at δ 2.33 ppm was assigned to the coordinated *o*-CH group of the aromatic ring.

For **5.16**, ^{1}H NMR spectroscopy in CD_2Cl_2 at ambient temperature shows broad resonances for the *o*-CH and CH_3-groups of the arene moiety due to dynamic exchange, while the remaining signals do not exhibit line broadening. Below 0 °C, the ^{1}H NMR spectrum is sharp and the number of resonances is consistent with the C_1 symmetric structure observed in the solid state. The *o*-protons of the pendant arene moiety are inequivalent and observed at δ 6.99 ppm and 5.25 ppm, compared to a single resonance at δ 6.96 ppm in **5.5**. The exchange between the *o*-H's can only occur by a process in which the arene at some stage is completely detached from the metal (Scheme 10).



Scheme 10

Exchange between these resonances was studied by variable temperature 2D EXSY NMR spectroscopy. Analysis of EXSY spectra obtained at four temperatures (8.3, -1.7, -12.0 and -22.0 ºC) gives the activation parameters for the process $\Delta H^{\ddagger} = 64(1)$ kJ·mol^{-1}K^{-1} and $\Delta S^{\ddagger} = 7(3)$ J·mol^{-1}·K^{-1}. The modest positive value for $\Delta S^{\ddagger}$ supports

the notion of at least partial detachment of the arene moiety in the transition state. These variable temperature ^{1}H NMR experiments allow the coalescence temperature for arene exchange to be determined and, furthermore, an independent determination of the free energy of activation $\Delta G^{\ddagger}$ for the process at the coalescence temperature.[21] Coalescence of the *ortho*-protons of the pendant arene moiety was obtained at 63 ºC in CD_2Cl_2 and gives the arene exchange activation energies of $\Delta G^{\ddagger}_{Tc}$ = 62 kJ·mol^{-1}.

Upon addition of the Lewis base THF-d_8 to the cationic species **5.16**, the pendant arene is released from the cationic vanadium center, as inferred from the single resonance for the two *o*-protons of the arene (δ 6.76 ppm) in [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)(THF)][$B(C_6F_5)_4$] (**5.18**). Furthermore, the *i*-Pr methine absorptions show typical shifts for a vanadium-THF adduct species (δ 5.50 and 3.90 ppm for **5.18**, δ 3.67 and 3.61 ppm for **5.16**). The transition between the arene coordinated species and the THF-adduct species is best observed in the ^{51}V NMR spectrum, where the environmental changes are easily seen at the metal center by the vanadium shift of the two species (δ -408.41 ppm for **5.16** and δ -383.05 ppm for **5.18**).

As the *o*-protons of the arene group of the Cp-arene ligand are the most accessible to the vanadium center, and the geometry for this interaction can be achieved more easily for the C_1 bridged system (*vide supra*), it is interesting to see whether the length of the bridge in the ligand will have an effect on this interaction. Therefore the cationic vanadium complex with an additional methylene (-CH_2) group in the bridge was generated. In an NMR tube, treatment of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.6**) with [Ph_3C][$B(C_6F_5)_4$] in dichloromethane at low temperature, generated quantitatively the cationic species [(η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)][$B(C_6F_5)_4$] (**5.17**) (Scheme 10). At low temperature (-10 ºC), the ^{1}H NMR spectrum of **5.17** shows two inequivalent signals for the arene *o*-CH at δ 6.95 ppm and 5.57 ppm and the absorption for the extra -CH_2 in the bridge appears as two doublets (each of 1H intensity). The C_2 bridged *ansa*-Cp-arene V(V) cation **5.17** is more thermally labile than its C_1 bridged analoge **5.16**. Upon standing at ambient temperature over 48 h, the ^{1}H NMR spectrum shows the gradual formation of other (as yet unidentified) diamagnetic species. This thermal lability suggests a weaker arene-metal interaction for the C_2 bridged *ansa*-Cp-arene V(V) cation **5.17** than for the C_1

bridged **5.16** (for a quantitative comparison, see below). As for **5.16**, the addition of THF-d_8 to **5.17** results in the formation of the THF-adduct and loss of the arene-metal interaction, as seen from the single resonance for the arene *o*-CH at δ 6.32 ppm.

The exchange between the inequivalent *o*-protons of the pendant arene moiety of the **5.17** species was studied by 2D EXSY spectroscopy. The EXSY spectra were recorded at four temperatures (-9.1, -19.6, -30.1 and -40.7 ºC) and analysis gives the following activation parameters for the process $\Delta H^{\ddagger}$ = 61(1) kJ·mol^{-1}K^{-1} and $\Delta S^{\ddagger}$ = 5(4) J·mol^{-1}·K^{-1}. Extrapolation to 63 ºC (the coalescence temperature of the C_1-bridged) gives an arene exchange activation energy of $\Delta G^{\ddagger}_{Tc}$ = 60 kJ·mol^{-1}, which is 2 kJ·mol^{-1} lower than for the C_1-bridged complex, suggesting a weaker interaction. For the C_2-bridge the coalescence of the *ortho*-protons of the pendant arene moiety occurred at 50 ºC in CD_2Cl_2 and gives the arene exchange activation energies of $\Delta G^{\ddagger}_{Tc}$ = 61 kJ·mol^{-1}.

Table 4. *Coalescence temperature and corresponding activation parameters for site exchange in **5.16** and **5.17**.*

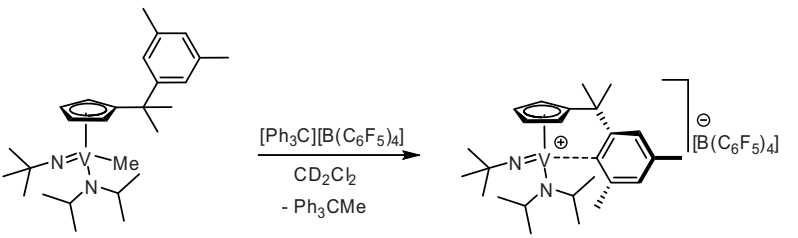
cation	*bridge*[*]	$\Delta H^{\ddagger}$ (kJ·mol^{-1}K^{-1})	$\Delta S^{\ddagger}$ (J·mol^{-1}K^{-1})	T_c (ºC)	$\Delta G^{\ddagger}_{Tc}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{63\,°C}$ (kJ mol^{-1})
5.16	C_1	64(1)	7(3)	63	62	62
5.17	C_2	61(1)	5(4)	50	61	60[#]

[*] C_1 = CMe_2, C_2 = CH_2CMe_2; [#] Calculated from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters.

The activation parameters for the dynamic exchange of compounds **5.16** and **5.17** are presented in Table 4. It confirms that the vanadium-arene interaction is weaker for the Cp-arene ligand with the C_2-bridge.

The behavior of the *ansa*-Cp-arene vanadium cationic species bearing a more electron donating group (*t*-Bu) on the imido functionality was also investigated. As the C_1 bridged system displays the stronger vanadium-arene interaction (*vide supra*), first the *t*-Bu-imido cationic vanadium species with the C_1 spacer was generated. Treatment of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(*t*-BuN)Me (**5.7**) with [Ph_3C][$B(C_6F_5)_4$] in dichloromethane-d_2 or bromobenzene-d_5 at ambient temperature generate the stable cationic vanadium species **5.19** (Scheme 11). The ^{1}H NMR spectrum shows, at room temperature, broadened absorptions for the *o*-

CH and ArMe of the pendant arene, but at low temperature (-20 ºC) η^1-arene coordination to the vanadium center is indicated by two separate singlets for the *o*-H atoms of the arene at δ 6.62 ppm and 4.64 ppm compared with one signal at δ 7.03 ppm in the starting material **5.7**.



5.7 **5.19**

Scheme 11

The exchange between the inequivalent *o*-protons of the pendant arene moiety of the **5.19** species was studied by 2D EXSY spectroscopy also. The EXSY spectra were recorded at five temperatures (-5, -15, -25, -35 and -45 ºC) and analysis gives the following activation parameters for the process $\Delta H^{\ddagger}$ = 57(1) kJ·mol^{-1}K^{-1} and $\Delta S^{\ddagger}$ = -6(2) J·mol^{-1}·K^{-1}. Extrapolation to 63 ºC (the coalescence temperature of the *p*-tolyl C_1-bridged) gives an arene exchange activation energy of $\Delta G^{\ddagger}_{Tc}$ = 59 kJ·mol^{-1}. In comparison with the C_1 *p*-tolyl complex **5.16**, the complex **5.19** having a more electron donating ligand (*t*-Bu) on the imido group, displays a weaker interaction between the pendant arene and the metal center (Table 5).

Table 5. *Coalescence temperature and corresponding activation parameters for site exchange in **5.16** and **5.19**.*

cation	*R-N=V*	$\Delta H^{\ddagger}$ (kJ·mol^{-1}K^{-1})	$\Delta S^{\ddagger}$ (J·mol^{-1}K^{-1})	T_c (ºC)	$\Delta G^{\ddagger}_{Tc}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{63\ ºC}$ (kJ mol^{-1})
5.16	*p*-tolyl	64(1)	7(3)	63	62	62
5.19	*t*-Bu	57(1)	-6(2)	50	59	59

The effect of enlarging the bridge of the pendant arene from CMe_2 to CH_2CMe_2 on the *t*-Bu-imido cationic species was investigated by treatment of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Me (**5.8**) with [Ph_3C][$B(C_6F_5)_4$] in dichloromethane. The expected cationic species could not be generated cleanly:

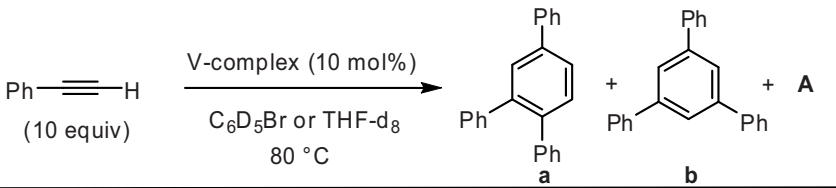
instead rapid decomposition followed (*in vacuo* transfer of the solvent reveals the presence of *N*-isopropyl-2-propanimine and diisopropyl amine in 1:1 ratio). In further attempts to generate the desired cationic species, other solvents (*e.g.* C_6D_5Br, toluene) and other activating reagents (*e.g.* $[PhNHMe_2][B(C_6F_5)_4]$) were screened, but with no success. Using a Lewis basic solvent (THF-d_8) and the $[Ph_3C][B(C_6F_5)_4]$ reagent, the THF-stabilized cationic vanadium species $[(\eta^5\text{-}C_5H_4CMe_2CH_2\text{-}3,5\text{-}Me_2C_6H_3)(i\text{-}Pr_2N)V^+(N\text{-}t\text{-}Bu)(THF)][B(C_6F_5)_4]^-$ (**5.20**) was obtained. According to ^1H NMR spectroscopy, the conversion to the cationic species is quantitative, with concomitant liberation of Ph_3CMe. The arene *o*-H exhibits one singlet (δ 6.39 ppm) and the *i*-Pr methine groups show typical shifts for a THF-adduct species: δ 5.59 and 3.98 ppm. Thus it appears that, with the more electron-donating *t*-Bu-imido group, the V-arene interaction for the ligand with the (less favorable) C_2 bridge is now too weak to stabilize the cationic species.

5.5 Reactivity of the cationic *ansa*-Cp-arene vanadium(V) amido-imido complexes

5.5.1 Reactivity towards phenylacetylene

In chapters 3 and 4 it was shown that electronically unsaturated vanadium species catalytically convert alkynes (phenylacetylene, diphenylacetylene) to yield mainly cyclotrimerization products. In the present section the activity of the cationic (η^1-Ar,η^5-Cp) vanadium system towards phenylacetylene was investigated. The *ansa*-Cp-arene vanadium cationic species **5.16**, **5.19** and **5.20** were treated with an excess of phenylacetylene in a ratio 10:1 (phenylacetylene:vanadium) and the reaction mixture was kept at 80 ºC for about 4 h. The mixtures were analyzed by gas chromatography (GC) and gas chromatography – mass spectrometry (GC-Ms). The results are shown in Table 6. All three cationic species tested form a mixture of the two phenylacetylene cyclotrimerization isomers (1,2,4- and 1,3,5-triphenylbenzene) in good yields, although side products were observed as well, especially when the **5.16** species was employed (see footnotes[22,23]).

Table 6. *Catalytic conversion of phenylacteylene by cationic ansa-Cp-arene vanadium species **5.16**, **5.19** and **5.20**.*



entry	V-complex	time (h)	alkyne *i* conv(%)	yield (%)	product ratio
1	**5.16***	3	95	82	**a**:**b** = 1:1.2
2	**5.19**	4	97	93	**a**:**b** = 1.4:1
3	**5.20**#	3	98	89	**a**:**b** = 1.5:1

* Cationic species crystallized out from dichloromethane-d_2 and redissolved in bromobenzene-d_5; # THF-d_8, arene is not coordinated; *i* determined by ^{1}H NMR; yield determined by GC analysis; A – represents formation of side products (ca. 12 % for **5.16**).[22,23]

In comparison with the non-substituted cyclopentadienyl cationic complex **2.6**, the *ansa*-Cp-arene vanadium cationic species **5.16** exhibits somewhat lower catalytic activity towards phenylacetylene, but with reasonable selectivity. The cationic species **5.19** and the THF-adduct **5.20** show also formation of cyclotrimerization products selectively, and the amount of side products is reduced.[23] The ^{1}H NMR spectra of the catalysis mixture of **5.20** and phenylacetylene showed the presence of *i*-Pr_2NH after 1 h at 80 ºC, as observed for the cationic non-substituted cyclopentadienyl species **2.5**.

5.5.2 Hydroamination reactions with the ansa-Cp-arene vanadium cationic species

In Chapter 4 the diisopropylamino ligand of the cationic species **2.6** was shown to be displaced by the *p*-toluidine via ligand exchange, generating a cationic species $[Cp(p\text{-tolylNH})V(N\text{-}p\text{-tolyl})(H_2N\text{-}p\text{-tolyl})]^+$ (**4.2**) which was then tested for catalytic hydroamination reactions. Applying the same principle, **5.16** was generated freshly and treated with an excess of *p*-toluidine (10 equiv/vanadium). After 1 h at room temperature the ^{1}H NMR spectrum in bromobenzene-d_5 shows two absorptions for the cyclopentadienyl group (δ 5.95 and 5.54 ppm), one absorption for the *o*-H of the arene, and an NH resonance at δ 12.55 ppm confirming the formation of the new species $[(\eta^5\text{-}C_5H_4CMe_2\text{-}3,5\text{-}Me_2C_6H_3)(p\text{-tolylNH})V(N\text{-}p\text{-tolyl})(H_2N\text{-}p\text{-tolyl})]^+$ (**5.21**) and, additionally free

diisopropylamine. The fact that the arene in **5.21** is not coordinating is a clear indication that *p*-toluidine is coordinated to the metal center.

Intermolecular hydroamination experiments were performed employing phenylacetylene and *p*-toluidine. The catalyzed reactions were carried out using 10 mol % of vanadium complex **5.21** and various molar ratios of phenylacetylene : *p*-toluidine, at 80 °C for 4 days. If the ratio employed is 1:1 (phenylacetylene: *p*-toluidine) then reactions proceed to give similar yields compared to the vanadium system **4.2** (Chapter 4) generating two major products: hydroamination Markovnikov-product and substituted quinoline. When increasing the phenylacetylene to *p*-toluidine ratio to 2:1 both products are still formed, but now in a 1:2 ratio (hydroamination product: quinoline). Thus, like **4.2** this catalyst system catalyzes the formation of quinolines and the amount of substituted quinoline can be increased by increasing the amount of phenylacetylene used; using higher ratios, *e.g.* 3:1 phenylacetylene : *p*-toluidine, did not increase the formation of quinolines any further, but led to the generation of alkyne cyclotrimerization products instead.

5.6 Concluding remarks

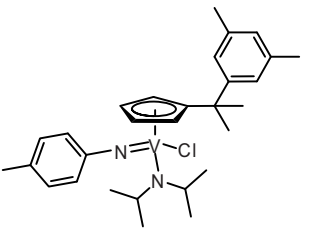
Generation of 16 v.e. vanadium cationic species from neutral Cp-arene amido imido methyl vanadium precursors **5.5** and **5.7** resulted in the coordination of the pendant arene in a η^1-fashion, stabilizing in this way the electronically unsaturated vanadium center. Compound **5.16** represents the first structural evidence for *ansa*-η^5,η^1-binding of a Cp-arene ligand to a metal center. This η^5,η^1-binding mode was observed for both *p*-tolyl-imido C_1 and C_2 bridged complexes. By introducing a more electron donating group (*t*-Bu) on the imido ligand, the electron density on the metal center increases, weakening the metal-arene dative interaction. Hence the η^5,η^1 coordination mode could be observed for the C_1-bridged compound whereas for the C_2- bridged it could not. The strength of vanadium – arene interaction was determined by variable-temperature and 2D NMR spectroscopy which allows for determination of the activation parameters for the process of arene dissociation. Changing from C_1-bridged to C_2-bridged compounds and from *p*-tolyl to *t*-Bu imido, the metal – arene interaction strength decreases. Preliminary experiments point toward (dynamic) intramolecular arene-vanadium interactions in the V(III) species generated in the thermolysis of **5.5** in the presence of the phosphines PMe_3 and dmpe.

5.7 Experimental section

Details about general synthetic and handling techniques, solvent purification and phosphorus compounds have been given in previous chapters. The compounds 6,6-dimethylfulvene[14], $[C_5H_4CMe_2$-3,5-$Me_2C_6H_3]Li$, $[C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3]Li(tmeda)$[12] and (*i*-$Pr_2N)VCl_2$(*t*-BuN)[24] were synthesized according to published procedures. The yields for compounds **5.11**, **5.13**, **5.14**, **5.15** were determined by ^1H NMR using Cp_2Fe as internal standard, weighing in a molar ratio 1:1 of Cp_2Fe:vanadium complex. The NMR data for the *i*-Pr_2NH and $(CH_3)_2C=N$(*i*-Pr) generated during the thermolysis process are given in Chapter 3. Variable temperature NMR spectra were recorded on a Varian Inova 500 spectrometer. Coalescence temperatures were determined on equilibrated samples (allowing ca. 10 min for the temperature to stabilize). Sample temperatures were determined using a Pt-100 resistance thermocouple that was inserted at the sample position in the probe. EXSY spectra were acquired using a modified NOESY pulse sequence (incorporating an additional *z*-gradient during mixing time τ_{mix}). In the indirectly detected dimension 256 complex points were collected with 2 scans and 2048 points per increment. Zero filling was applied to obtain 2048 x 2048 data points, and Gaussian line-broadening was applied in both dimensions prior to Fourier transformation. Integration of the EXSY spectra recorded at four different temperatures with four mixing times was performed using the Gaussian fit routine implemented in Sparky.[25] Using Mathematica 5.2,[26] cross-peak volumes of the spectra were normalized (I_x/I_d) and the data points were fitted against equation (1)[27] by non-linear regression.

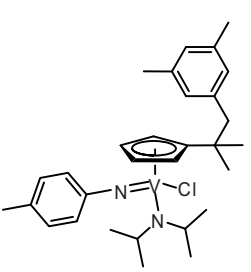
$$I_x/I_d = (1-e^{-2k\tau mix})/(1+e^{-2k\tau mix}) \quad \text{with} \quad k=(k_bT/h)\exp(-\Delta G^{\#}/RT) \qquad (1)$$

Synthesis of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-*t*olyl)Cl (5.1)



Onto a mixture of (*i*-Pr_2N)V(*p*-tolylN)Cl_2[24] (1.50 g, 4.58 mmol) and Li[$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$] (1.00 g, 4.58 mmol), 100 mL of THF was condensed at liquid nitrogen temperature. The mixture was warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the red residue was stripped twice with 5 mL of pentane. Repeated extraction with 50 mL of pentane and subsequent cooling to –25 ºC yielded 1.90 g (3.53 mmol, 77%) of compound **5.1**. The red needles thus obtained were suitable for X-ray analysis. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 7.19 (d, J_{HH} = 8.2 Hz, 2H, CH *p*-tolylN), 6.97 (s, 2H, Ar *o*-H), 6.76 (d, J_{HH} = 8.2 Hz, 2H, CH *p*-tolylN), 6.65 (s, 1H, Ar *p*-H), 6.32 (dt, J_{HH} = 3.4 , 2.1, 1H Cp), 5.91 (td, J_{HH} = 2.1, 3.1 Hz, 1H Cp), 5.79 (dt, J_{HH} = 3.4, 2.1 Hz, 1H Cp), 5.51 (td, J_{HH} = 2.1, 3.1 Hz, 1H Cp), 5.01 (sept. , J_{HH} = 6.23 Hz, 1H, C*H* *i*-Pr), 3.34 (sept., J_{HH} = 6.23 Hz, 1H, C*H* *i*-Pr), 2.10 (s, 6H, CH_3 Ar), 2.0 (s, 3 H, CMe_2), 1.98 (s, 3 H, CMe_2), 1.79 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 1.73 (s, 3H, CH_3 *p*-tolylN), 1.28 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 1.04 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 0.75 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6 25 °C): δ 152 (*C ipso* Ar), 137.6 (*C ipso p*-tolyl), 137.3 (*C ipso* Ar) , 135.8 (*C ipso p*-tolyl), 129.2 (CH *p*-tolylN), 127.6 (Ar *p*-CH), 126.3 (CH *p*-tolylN), 124.9 (Ar *o*-CH), 114.4 (Cp CH), 108.7 (Cp CH), 107 (Cp CH), 101.6 (Cp CH), 65.6 (CH *i*-Pr), 59.7 (*C*H *i*-Pr), 41.06 (C-bridge Ar-Cp), 30.7 (*C*H_3 *i*-Pr), 29.39 (CH_3 *p*-tolylN), 26.98 (CH_3 *i*-Pr), 21.4 (CH_3 Ar), 21.19 (CMe_2), 19.22 (CH_3 *i*-Pr), 17.25 (CH_3 *i*-Pr). Anal. Calcd for $C_{29}H_{40}N_2VCl$: C, 69.24; H, 8.02; N, 5.57. Found: C, 69.20 H, 8.06; N, 5.64.

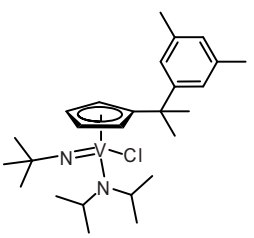
Synthesis of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)VCl(*p*-tolylN) (5.2)



Onto a mixture of (*i*-Pr_2N)V(N-*p*-tolyl)Cl_2[24] (0.80 g, 2.45 mmol) and Li[$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$](tmeda) (0.85 g, 2.45 mmol), 50 mL of THF was condensed at liquid nitrogen temperature. The mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed *in vacuo*, and the red oily residue was stripped twice with 5 mL pentane. After extraction with 30 mL of pentane, the extract was filtered off; the solvent was removed *in vacuo* to yield

1.01 g (1.97 mmol, 80%) of compound **5.2** as a red oil. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 7.21 (d, J_{HH} = 8.3 Hz, 2H CH *p*-tolylN), 6.76 (d, J_{HH} = 8.5 Hz, 3H CH *p*-tolylN overlap with 1H Ar), 6.51 (s, 2H CH Ar), 6.07 (td, J_{HH} = 3.5, 2.1 Hz, 1H Cp), 5.82 (dt, J_{HH} = 3.1, 2.4 Hz, 1H Cp), 5.72 (td, J_{HH} = 3.0, 2.1 Hz, 1H Cp), 5.55 (td, J_{HH} = 2.9, 2.1 Hz, 1H Cp), 5.04 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 3.36 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 2.76 (d, J_{HH} = 13.28 Hz, 1H CH_2-bridge), 2.72 (d, J_{HH} = 13.26 Hz, 1H CH_2-bridge), 2.16 (s, 6H CH_3-Ar), 2.01 (s, 3H CH_3 *p*-tolyl), 1.79 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.46 (s, 3H CMe_2), 1.33 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 1.30 (s, 3H CMe_2), 1.04 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.78 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6 , 25 ^{0}C): δ 138.78 (*ipso*-C), 137.61 (*ipso*-C), 136.68 (*ipso*-C), 135.82 (*ipso*-C), 129.27 (*ipso*-C Cp), 129.24 (CH Ar), 129.12 (CH *p*-tolylN), 127.89 (CH *p*-tolylN), 125.65 (CH Ar), 112.70 (CH Cp), 108.77 (CH Cp), 104.97 (CH Cp), 101.19 (CH Cp), 65.39 (CH *i*-Pr), 58.98 (CH *i*-Pr), 52.41 (CH *C*H_2-bridge), 37.46 (C-bridge Ar-Cp), 31.22 (CH_3 *i*-Pr), 27.71(CH_3 *p*-tolylN), 27.36 (C*Me*$_2$), 27.31 (C*Me*$_2$), 21.39 (CH_3 Ar), 21.16 (CH_3 *i*-Pr), 19.42(CH_3 *i*-Pr), 17.40(CH_3 *i*-Pr).

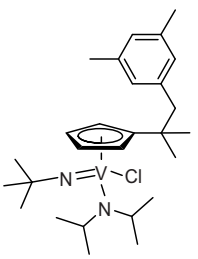
Synthesis of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Cl (5.3)



THF (50 mL) was condensed at liquid nitrogen temperature onto a mixture of (*i*-Pr_2N)V(N-*t*-Bu)Cl_2 (0.95 g, 3.24 mmol) and of Li[$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$] (0.70 g, 2.45 mmol). The mixture was allowed to warm up to room temperature and stirred overnight. The solvent was removed *in vacuo*, and residual THF removed by stirring with 10 mL pentane, which was subsequently pumped off. The mixture was extracted with 30 mL of pentane which subsequently was removed *in vacuo* yielding compound **5.3** (1.27 g, 2.71 mmol, 84%) as a red solid. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 7.08 (s, 2H Ar), 6.71 (s, 1H Ar), 5.89 (dd, J_{HH} = 5.2, 2.2 Hz, 1H Cp), 5.84 (dd, J_{HH} = 5.3, 2.2 Hz, 1H Cp), 5.81 (dd, J_{HH} = 5.4, 2.8 Hz, 1H Cp), 5.69 (dd, J_{HH} = 5.3, 3.0 Hz, 1H Cp), 4.94 (sept., J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 3.30 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 2.19 (s, 6H CH_3-Ar), 2.07 (s, 3H CMe_2), 1.93 (s, 3H CMe_2), 1.78 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.25 (s, 9H CH_3 *t*-BuN), 1.24 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.00 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.77 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (125.7 MHz, C_6D_6, 25 °C): δ 152.16 (*ipso*-C Ar), 137.33 (*ipso*-C Ar), 127.61 (*C*H Ar), 124.36 (*C*H Ar), 106.85 (*C*H Cp), 105.37 (*C*H Cp), 102.69 (*C*H Cp), 100.94

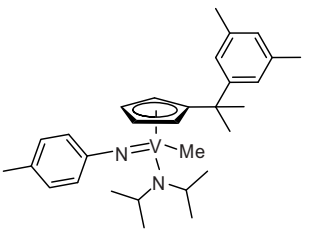
(*C*H Cp), 65.21 (*C*H *i*-Pr), 56.37 (*C*H *i*-Pr), 40.57 (C_q-bridge Ar-Cp), 31.26 (CH_3 Ar), 31.17 (CH_3 *t*-BuN), 29.00 (CMe_2), 28.29 (CMe_2), 27.46 (CH_3, *i*-Pr), 21.73 (CH_3, *i*-Pr), 19.41 (CH_3, *i*-Pr), 17.83 (CH_3, *i*-Pr), C_q of *t*-BuN not observed. Anal. Calcd.(%) for $C_{26}H_{42}N_2VCl$: C, 66.58; H, 9.03; N, 5.97. Found: C, 66.43; H, 8.89; N, 5.91.

Synthesis of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Cl (5.4)



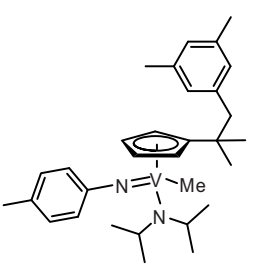
Onto a mixture of (*i*-Pr_2N)V(N-*t*-Bu)Cl_2 (0.40 g, 1.36 mmol) and Li[$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$] (0.48 g, 1.36 mmol), 50 mL of toluene was condensed at liquid nitrogen temperature. The reaction mixture was allowed to warm up to room temperature and stirred overnight resulting in a wine red solution. The solvent was removed *in vacuo*, and residual toluene was removed by stirring with 10 mL pentane, which was subsequently pumped off. Extraction with 30 mL of pentane and removal of the solvent *in vacuo*, yielded pure compound **5.4** (0.55 g, 1.14 mmol, 84 %) as a red foam. Recrystalization from pentane at – 30 °C gave red crystals suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 6.78 (s, 1H Ar), 6.62 (s, 2H Ar), 5.74-5.66 (m, 3H Cp), 5.61 (dd, J_{HH} = 4.2, 2.1 Hz, 1H Cp), 4.95 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 3.30 (sept., J_{HH} = 6.6 Hz, 1H CH *i*-Pr), 2.88 (d, *J* = 12.08 Hz, 1H CH_2-bridge), 2.85 (d, *J* = 12.91 Hz, 1H CH_2-bridge), 2.20 (s, 6H CH_3-Ar), 1.78 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.60 (s, 3H CMe_2), 1.53 (s, 3H CMe_2), 1.25 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 1.24 (s, 9H CH_3 *t*-BuN, overlap with CH_3 *i*-Pr), 0.99 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.77 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (125.7 MHz, C_6D_6, 25 °C): δ 138.84 (*ipso*-C Ar), 136.67(*ipso*-C Ar), 129.23 (CH Ar), 127.91 (CH Ar), 106.09 (CH Cp), 105.77 (CH Cp), 101.43 (CH Cp), 100.27 (CH Cp), 65.10 (*C*H *i*-Pr), 56.23 (*C*H *i*-Pr), 52.70 (CH CH_2-bridge), 37.68 (C_q-bridge Ar-Cp), 31.32 (CH_3 Ar), 31.19 (CH_3 *t*-BuN), 27.42 (CMe_2), 26.71 (CH_3, *i*-Pr), 26.60 (CMe_2), 21.41 (CH_3, *i*-Pr), 19.37 (CH_3, *i*-Pr), 17.76 (CH_3, *i*-Pr), C_q of *t*-BuN not observed. Anal. Calcd.(%) for $C_{27}H_{42}N_2VCl$: C, 67.42; H, 8.80; N, 5.82. Found: C, 67.10; H, 9.2, N 5.83.

Synthesis of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (5.5)



To a cold solution (-40 ºC) of **5.1** (1.08 g, 2.15 mmol) in Et_2O (30 mL), MeLi (1.36 mL, 2.15 mmol, 1.58 M in ether) was added slowly via a dropping funnel. The mixture was stirred at -40 ºC for 1.5 h and then slowly warmed to -10 ºC. The solvent was removed *in vacuo* and the solid was stripped with 5 mL of pentane. Repeated extraction with 20 mL of cold (-10 ºC) pentane, followed by concentration of the solvent and subsequent cooling to –35 ºC yielded 0.65 g (1.35 mmol, 70 % yield) red crystals of compound **5.5**. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 7.19 (d, J_{HH} = 8.1 Hz, 2H, CH *p*-tolylN), 6.96 (s, 2H, Ar *o*-H), 6.87 (d, J_{HH} = 8.1 Hz, 2H, CH *p*-tolyl), 6.65 (s, 1H, Ar *p*-H), 5.78 (dt, J_{HH} = 3.4, 2.1, 1H Cp), 5.69 (td, J_{HH} = 2.1, 3.1 Hz, 1H Cp), 5.64 (dt, J_{HH} = 3.4, 2.1 Hz, 1H Cp), 5.56 (td, J_{HH} = 2.1, 3.1 Hz, 1H Cp), 4.48 (sept. , J_{HH} = 6.3 Hz, 1H, CH *i*-Pr), 3.29 (sept, J_{HH} = 6.3 Hz, 1H, CH *i*-Pr), 2.11 (s, 6H, CH_3 Ar), 1.72 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 1.67 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 1.64 (s, 3H, CMe_2), 1.61 (s, 3 H, CMe_2), 1.13 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 0.84 (d, J_{HH} = 6.3 Hz, 3H, CH_3 *i*-Pr), 0.82 (s, 3H V-CH_3). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6 , 25 °C): δ 151.45 (C *ipso* Ar), 137.33 (C *ipso p*-tolyl), 133.48 (Ar, C *ipso*), 132.06 (C *ipso p*-tolyl), 129.15 (CH *p*-tolyl), 127.60 (CH *p*-tolyl), 125.81 (CH, Ar), 124.18 (CH, Ar), 111.86 (CH, Cp), 106.17 (CH, Cp), 105.35 (CH, Cp), 103.90 (CH, Cp), 62.71 (CH *i*-Pr), 55.29 (CH *i*-Pr), 41.06 (C-bridge Ar-Cp), 32.50 (CH_3 *i*-Pr), 30.98 (CMe_2) 30.83 (CMe_2), 27.20 (CH_3 *i*-Pr), 21.61(CH_3 Ar) 21.12 (CH_3 *p*-TolylN), 20.77 (CH_3 *i*-Pr), 19.01 (CH_3 *i*-Pr), V-CH_3 not observed. ^{51}V NMR (131.4 MHz, CD_2Cl_2, 25 ºC) δ: -559.77. ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -556.48. Anal. Calcd.(%) for $C_{30}H_{43}N_2V$: C, 74.66; H, 8.98; N, 5.80. Found: C, 74.6; H, 9.15; N, 5.65.

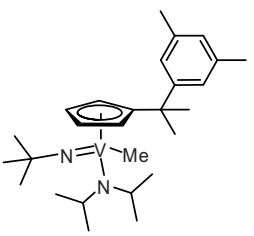
Synthesis of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (5.6)



At -50 ºC MeLi (1.15 mL, 1.97 mmol, 1.6 M in ether) was added slowly to a solution of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Cl (**5.2**) (1.02 g, 1.97 mmol) in 50 mL of Et_2O. The mixture was slowly warmed up to -10 ºC and stirred at this temperature for 2 hours. The solvent was removed *in vacuo* at -10 ºC and the solid was stripped with cold pentane (5 mL). Extraction with 20 mL

of cold (-10 ºC) pentane, followed by concentration of the solvent and stored at (-80 ºC) yielded 0.75 g (1.51 mmol, 76 %) of compound **5.6** as red-brown foam. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 6.98 (s, 4H *p*-tolyl), 6.78 (s, 1H *p*-Ar), 6.39 (s, 2H, *o*-Ar), 5.82 (dd, J_{HH} = 5.0, 2.7 Hz, 1H Cp), 5.72 (dd, J_{HH} = 4.9, 2.8 Hz, 1H Cp), 5.61 (dd, J_{HH} = 4.8, 2.0 Hz, 1H Cp), 5.46 (dd, J_{HH} = 4.9, 1.9 Hz, 1H Cp), 4.64 (sept, J_{HH} = 6.6 Hz, 1H CH *i*-Pr), 3.47 (m, 1H, CH *i*-Pr), 2.63 (d, J = 12.91 Hz, 1H CH_2-bridge), 2.59 (d, J = 12.43 Hz, 1H CH_2-bridge), 2.30 (s, 3H, CH_3 *p*-tolylN), 2.20 (s, 6H, CH_3-Ar), 1.59 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 1.57 (d, J_{HH} = 6.4 Hz, 3H, CH_3 *i*-Pr), 1.07 (s, 3 H, CMe_2), 1.07 (d overlap with CMe_2, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.04 (s, 3 H, CMe_2), 0.92 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 0.38 (s, 3H, V-Me). ^{13}C {^{1}H} NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ 138.89 (*ipso*-C Ar), 136.84 (*ipso*-C *p*-tolylN), 133.56 (*ipso*-C Ar), 131.55 (*ipso*-C *p*-TolylN), 129.0 (CH *p*-tolylN), 128.85 (2CH Ar), 127.51 (CH *p*-tolylN), 125.63 (CH Ar), 111.57 (CH, Cp), 105.89 (CH, Cp), 104.56 (CH, Cp), 103.44 (CH, Cp), 62.93 (CH *i*-Pr), 55.22 (CH *i*-Pr),51.98 (CH CH_2-bridge), 36.35 (C-bridge Ar-Cp), 32.52 (CH_3 *i*-Pr), 28.48 (CMe_2), 28.09 (CMe_2), 26.96 (CH_3 *i*-Pr), 21.28 (CH_3 CH_3-Ar), 21.18 (CH_3 *i*-Pr), 20.94 (CH_3 *p*-TolylN), 19.08 (CH3 i-Pr), V-Me not observed. ^{51}V NMR (131.4 MHz, CD_2Cl_2, 25 ºC) δ: -560.91. Anal. Calcd.(%) for $C_{31}H_{45}N_2V$: C, 74.8; H, 8.79; N, 5.82. Found: C, 74.1; H, 8.62; N, 5.73.

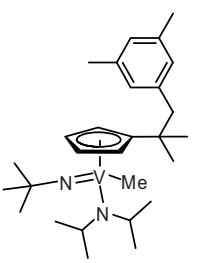
Synthesis of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Me (5.7)



MeLi (1.70 mL, 1.6 M, 2.71 mmol) was added to a cold solution (-40 ºC) of **5.3** (1.27 g, 2.71 mmol) in diethylether (30 mL). The mixture was stirred at -10 ºC for 1 h. The solvent was removed *in vacuo* at this temperature and the solid was stripped with cold pentane (5 mL). Repeated extraction with 20 mL of cold (-10 ºC) pentane and subsequent cooling to – 30 ºC yielded compound **5.7** (0.91 g, 2.03 mmol, 80.5 %) as a green-yellow solid. ^{1}H NMR (400 MHz, C_6D_6 25 °C): δ 7.03 (s, 2H *o*-Ar), 6.71 (s, 1H *p*-Ar), 5.73 (td, J_{HH} = 2.8, 1.7 Hz, 1H Cp), 5.68 (td, J_{HH} = 3.9, 1.9 Hz, 1H Cp), 5.65 (td, J_{HH} = 3.1, 2.0 Hz, 1H Cp), 5.50 (dd, J_{HH} = 5.1, 2.8 Hz, 1H Cp), 4.45 (sept, J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 3.26 (sept, J_{HH} = 5.9 Hz, 1H CH *i*-Pr), 2.17 (s, 6H CH_3-Ar), 1.77 (s, 3H CMe_2), 1.72 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.64 (s, 3H CMe_2), 1.57 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 1.28 (s, 9H CH_3 *t*-BuN), 0.86 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr), 0.85 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 0.63 (s, 3H V-

Me). ^{13}C {^{1}H}NMR (125.7 MHz, C_6D_6, 25 °C): δ 151.46 (*ipso*-C Ar), 137.33 (CH Ar), 127.66 (*ipso*-C Ar), 124.37 (CH Ar), 108.64 (CH Cp), 108.31 (CH Cp), 107.94 (CH Cp), 100.56 (CH Cp), 62.66 (*C*H *i*-Pr), 53.29 (*C*H *i*-Pr), 38.64 (C_q-bridge Ar-Cp), 32.55 (CH_3, *i*-Pr), 31.74 (CH_3, *i*-Pr), 31.72 (CH_3 Ar), 31.66 (CH_3 *t*-BuN), 27.61 (CMe_2), 21.69 (CMe_2), 20.62 (CH_3, *i*-Pr), 19.24(CH_3, *i*-Pr), V-Me and C_q of *t*-BuN not observed. ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -623.01. Anal. Calcd.(%) for $C_{27}H_{45}N_2V$: C, 72.29; H, 10.11; N, 6.24. Found: C, 71.27; H, 10.07; N, 6.00.

Synthesis of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)Me (5.8)



At -40 °C, MeLi (0.6 mL, 1.6 M, 0.95 mmol) was slowly added via a dropping funnel to a solution of **5.4** (0.46 g, 0.95 mmol) in diethylether (50 mL). The mixture was warmed up to -10 °C and stirred for 2 h at this temperature. The color of the solution changed from red to yellowish brown. The work up procedure was done at -10 °C. After removal of the solvent *in vacuo*, the residual ether was stripped by addition of 2 x 5 mL of cold pentane. Extraction of the reaction mixture with 50 mL of cold pentane and removal of solvent *in vacuo* at -10 °C yielded **5.8** (0.35 g, 0.76 mmol, 80 %) as a brown-green oil. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.78 (s, 1H *p*-Ar), 6.57 (s, 2H *o*-Ar), 5.60-5.56 (m, 2H Cp), 5.47 (dd, J_{HH} = 5.2, 2.9 Hz, 1H Cp), 5.42 (td, J_{HH} = 3.3, 2.1 Hz, 1H Cp), 4.39 (sept., J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 3.22 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 2.76 (d, J_{HH} = 12.59 Hz, 1H CH_2-bridge), 2.72 (d, J_{HH} = 12.63 Hz, 1H CH_2-bridge), 2.21 (s, 6H CH_3 Ar), 1.70 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.52 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 1.34 (s, CH_3 CMe_2), 1.28 (s, 9H CH_3 *t*-BuN), 1.21 (s, CH_3 CMe_2), 0.83 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.82 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 0.60 (s, 3H CH_3 V-Me). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -627.16. ^{1}H NMR (400 MHz, C_6D_5Br, 25 °C): δ 6.74 (s, 1H Ar), 6.52 (s, 2H Ar), 5.62 (dt, J_{HH} = 3.0, 2.1 Hz, 1H Cp), 5.59 (td, J_{HH} = 3.4, 2.0 Hz, 1H Cp), 5.47 (dt, J = 2.9, 2.2 Hz, 1H Cp), 5.44 (td, J = 3.4, 2.1 Hz, 1H Cp), 4.43 (sept., J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 3.24 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 2.71 (d, J_{HH} = 3.0 Hz 2H CH_2-bridge), 2.23 (s, 6H CH_3 Ar), 1.65 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.49 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 1.32 (s, CH_3 CMe_2), 1.27 (s, 9H CH_3 *t*-BuN), 1.18 (s, CH_3 CMe_2), 0.88 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 0.84 (d, J_{HH} = 6.6 Hz, 3H CH_3 *i*-Pr), 0.46 (s, 3H CH_3 V-Me). ^{13}C {^{1}H}NMR (100 MHz, C_6D_5Br, 25 °C): δ 138.43 (*ipso*-C Ar),

136.14 (*ipso*-C Ar), 128.63 (CH Ar), 127.52 (CH Ar), 107.90 (CH Cp), 107.25 (CH Cp), 106.78 (CH Cp), 99.31 (CH Cp), 62.09 (*C*H *i*-Pr), 52.63 (*C*H *i*-Pr), 52.28 (CH CH_2-bridge), 35.20 (C_q-bridge Ar-Cp), 32.28 (CH_3, *i*-Pr), 31.31 (CH_3 *t*-BuN), 29.13 (CH_3 Ar), 27.79 (CMe_2), 27.14 (CMe_2), 21.22 (CH_3, *i*-Pr), 20.22 (CH_3, *i*-Pr), 18.93 (CH_3, *i*-Pr), V-Me and C_q of *t*-BuN not observed. Anal. Calcd.(%) for $C_{28}H_{47}N_2V$: C, 72.69; H, 10.24; N, 6.06. Found: C, 69.74; H, 10.15; N, 5.94.

Thermolysis of compound 5.5

A solution of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.5**) (0.03 g, 0.06 mmol) in 0.5 mL C_6D_6 was heated at 50 °C over a period of 48 h after which the thermal decomposition was complete. ^{1}H NMR spectrum shows methane liberation, *N*-isopropyl-2-propanimine, diisopropyl amine and the dimeric vanadium compound [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)V(N-*p*-tolyl)Me]$_2$. Typical ^{1}H NMR resonances for this species are δ: -0.84 ppm (V-Me), 2.05 (Me *p*-tolyl), 2.19 (Me-Ar), 5.88 and 5.35 (CH Cp). Additionally, the ^{1}H NMR spectrum of the mixture shows broad resonances over a broad range: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 46.82 (br, $\Delta\nu_{1/2}$ = 195 Hz), 38.65 (br, $\Delta\nu_{1/2}$ = 1056 Hz), 32.29 (br, $\Delta\nu_{1/2}$ = 225 Hz), 17.51 (br, $\Delta\nu_{1/2}$ = 123 Hz), 9.18 (br, $\Delta\nu_{1/2}$ = 48 Hz), 3.84 (br, $\Delta\nu_{1/2}$ = 30 Hz), 2.70 (br, $\Delta\nu_{1/2}$ = 16 Hz), -3.13 (br, $\Delta\nu_{1/2}$ = 22 Hz), -7.02 (br, $\Delta\nu_{1/2}$ = 177 Hz), -7.85 (br, $\Delta\nu_{1/2}$ = 60 Hz), -25.84 (br, $\Delta\nu_{1/2}$ = 123 Hz). The amount of *N*-isopropyl-2-propanimine and diisopropyl amine was determined by using Cp_2Fe as internal standard (80 % and 20% respectively); the two organic products were isolated by vacuum distillation and identified by ^{1}H NMR[28] and GC-Ms analysis (m/z = 101, respective m/z = 99). For determination of the methane evolved: the NMR tube was attached to the vacuum line, frozen in liquid nitrogen and evacuated three times after which the tube was placed in the oven at 50 ºC. After the decomposition is complete the tube is attached again to the vacuum line and the amount of methane formed in the reaction was determined using a Toepler pump [0.80 CH_4/V].

Thermolysis of compound 5.6

A solution of (η^5-$C_5H_4CMe_2$-CH_2-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)Me (**5.6**) (0.03 g, 0.060 mmol) in 0.5 mL C_6D_6 or THF-d_8 was thermolyzed at 50 °C over a period of 36 h. The NMR data show formation of methane, *N*-isopropyl-2-propanimine, diisopropyl amine and the dimeric vanadium complex [(η^5-$C_5H_4CMe_2CH_2$-3,5-

$Me_2C_6H_3$)V(N-*p*-tolyl)Me]$_2$. Surprisingly the final mixture does not contain broad paramagnetic species on such a wide range as **5.5**. Broad signals: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.87 (br, $\Delta\nu_{1/2}$ = 49 Hz), 4.71 (br, $\Delta\nu_{1/2}$ = 45 Hz). *N*-isopropyl-2-propanimine and disopropyl amine were isolated by vacuum distillation and identified by ^{1}H NMR[28] and GC-Ms analysis. The amount of methane was measured by Toepler pump [0.70 CH_4/V] as mention for compound **5.5** (*vide supra*). ^{1}H NMR data for *i*-Pr_2NH (400 MHz, CD_2Cl_2, 25 °C): δ 2.87 (sept, J_{HH} = 6.2 Hz, 2H CH *i*-Pr_2N), 0.99 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), 0.38 (s broad, 1H NH). (400 MHz, THF-d_8, 25°C): δ 2.84 (sept, J_{HH} = 6.21 Hz, 2H CH *i*-Pr_2N), 0.94 (d, J_{HH} = 6.2 Hz, 12H, CH_3 *i*-Pr_2N), NH not observed.

^{1}H NMR for $(CH_3)_2$C=N(*i*-Pr) (400 MHz, CD_2Cl_2, 25°C): δ 3.57 (sept, J_{HH} = 6.2 Hz, 1H CH *i*-Pr_2N), 1.91 (s, 3H CH_3), 1.80 (s, 3H CH_3), 1.05 (d, J_{HH} = 6.2 Hz, 6H, CH_3 *i*-Pr_2N). (400 MHz, THF-d_8, 25°C): δ 3.57 (sept, overlap with the solvent 1H CH *i*-Pr_2N), 1.85 (s, 3H CH_3), 1.75 (s, 3H CH_3), 0.99 (d, J_{HH} = 6.2 Hz, 6H, CH_3 *i*-Pr_2N).

Data for dimer [(η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)V(N-*p*-tolyl)Me]$_2$: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.98 (d, *J* = 7.93 Hz, 2H CH *p*-tolylN), 6.78 (d, *J* = 8.01 Hz, 2H CH *p*-tolylN), 6.75 (s, CH Ar), 6.66 (s, CH Ar), 5.84 (t, *J* = 2.45 Hz 2H Cp), 5.37 (t, *J* = 2.44 Hz 2H Cp), 2.69 (s, 2H CH_2-bridge), 2.17 (s, 6H CH_3-Ar), 1.11 (s, 6H CH_3-bridge), -0.86 (s, 3H V-Me). ^{1}H NMR (400 MHz, THF-d_8, 25°C): δ 7.02 (d, *J* = 7.8 Hz, 2H CH *p*-tolylN), 6.40 (d, *J* = 7.9 Hz, 2H CH *p*-tolylN), 6.61 (s, CH Ar), 6.43 (s, CH Ar), 5.83 (br, 2H CH Cp), 5.29 (br, 2H CH Cp), 2.62 (s, 2H CH_2-bridge), 2.16 (s, 6H CH_3-Ar), 1.28 (s, 6H CH_3-bridge), -1.12 (s, 3H V-Me). (400 MHz, CD_2Cl_2, 25 °C): δ 7.22 (d, *J* = 7.93 Hz, 2H CH *p*-tolylN), 6.98 (s, 1H CH Ar), 6.96 (d, *J* = 8.20 Hz, 2H CH *p*-tolylN), 6.78 (s, 1H CH Ar), 6. 46 (s, 1H CH Ar), 6.19 (t, *J* = 2.61 Hz 2H Cp), 4.44 (t, *J* = 2.45 Hz 2H Cp), 2.87 (s, 2H CH_2-bridge), 2.42 (s, 3H CH_3 *p*-tolylN), 2.17 (s, 6H CH_3-Ar), 1.42 (s, 6H CH_3-bridge).

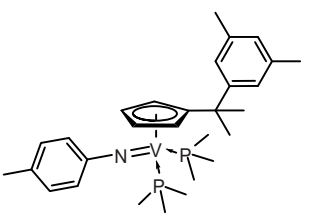
Thermolysis of compounds 5.7 and 5.8

a) A solution of **5.7** (0.03 g, 0.06 mmol) in 0.5 mL C_6D_6 was thermolyzed at 50 °C over a period of 30 h, after which the starting material was fully converted. The NMR data show formation of methane (0.91 CH_4/V by Toepler pump), *N*-isopropyl-2-propanimine, diisopropyl amine, plus diamagnetic signals in the cyclopentadienyl area (^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.10 (Cp, 2H), 5.84

(Cp, 1H), 5.80 (Cp, 1H), 5.72 (Cp, 1H), 5.67 (Cp, 2H), 5.57 (Cp, 1H), 5.55 (Cp), 5.41 (Cp)) together with broad signals (^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 16.13 (br, $\Delta\nu_{1/2}$ = 463 Hz), 10.84 (br, $\Delta\nu_{1/2}$ = 603 Hz), 7.92 (br, $\Delta\nu_{1/2}$ = 126 Hz)). The volatiles were vacuum transferred and the remaining crude mixture was redissolved in C_6D_6 (not everything is soluble in benzene) but unfortunately the remainder of the reaction mixture is intractable. The Toepler pump experiment was performed as previously presented for compound **5.5** (*vide supra*).

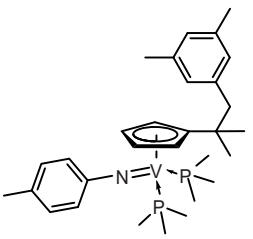
b) A solution of **5.8** (0.05 g, 0.11 mmol) in 0.5 mL C_6D_6 was thermolyzed at 50 °C over a period of 60 h, after which the NMR data show formation of methane (0.90 CH_4/V by Toepler pump), *N*-isopropyl-2-propanimine and diisopropyl amine; after this time at 50 °C, solid has formed in the NMR tube. ^{1}H NMR spectroscopy in C_6D_6 of the soluble species show in the aromatic area resonances of diamagnetic species at δ ppm: 6.78, 6.74, 6.69, 6.60, 6.50 (overlap with a broad signal), 6.11 (broad), 5.75 (Cp), 5.43 (Cp), 5.30 (Cp), 5.18 (Cp). The broad signals were recorded at: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 15.85 (br, $\Delta\nu_{1/2}$ = 520 Hz), 10.9 (br, $\Delta\nu_{1/2}$ = 306 Hz), 6.11 br, $\Delta\nu_{1/2}$ = 120 Hz).

Generation of (η^5-$C_5H_4CMe_2$-3,5-Me_2-C_6H_3)V(N-*p*-tolyl)(PMe_3)$_2$ (5.11)



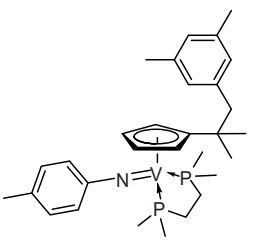
In an NMR tube experiment, PMe_3 was added (0.006 g, 0.008 mL, 0.08 mmol) to a solution of **5.5** (0.02 g, 0.04 mmol) in C_6D_6 (0.5 mL). The tube was attached to a vacuum line, frozen in liquid nitrogen and degassed, after which it was put at 50 °C and kept at this temperature for 8 days. After this time the amount of methane was measured by Toepler pump [0.92 CH_4/V], and the volatiles were transferred *in vacuo* and analyzed by ^{1}H NMR and GC-Ms. The analysis confirmed the presence of *N*-isopropyl-2-propanimine. The compound **5.11** was generated in 92% yield considering the gas balance and Cp_2Fe as internal standard. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ 7.38 (s, 2H *o*-CH Ar), 7.25 (broad, 2H CH *p*-tolylN), 6.98 (broad, 2H CH *p*-tolylN), 6.76 (s, 1H *p*-CH Ar), 5.34 (br, 2H CH Cp, $\Delta\nu_{1/2}$ = 70 Hz), 4.39 (br, 2H CH Cp, $\Delta\nu_{1/2}$ = 40 Hz), 2.23 (s, 3H Me *p*-tolylN), 2.15 (broad, 6H Me-Ar), 1.41 (s, 6H CMe_2), 1.04 (s, 18H PMe_3), 0.78 (s, free PMe_3). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: 265.96. ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25 ºC): δ 52.70 (plateau, $\Delta\nu_{top}$ = 2659), -58.50 (broad s, free PMe_3).

Generation of (η^5-$C_5H_4CMe_2CH_2$-3,5-Me_2-C_6H_3)V(N-*p*-tolyl)(PMe_3)$_2$ (5.12)



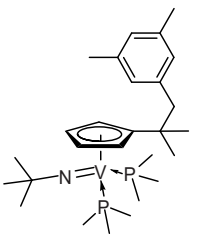
In an NMR tube experiment, PMe_3 was added (0.007 g, 0.009 mL, 0.09 mmol) to a solution of **5.6** (0.03 g, 0.05 mmol) in C_6D_6 (0.5 mL). The tube was kept for 6 days at 50 °C after which all the starting material was converted into **5.12**. ^{1}H NMR (500 MHz, C_6D_6, 25 ºC): δ 7.16 (d, J_{HH} = 7.9 Hz 2H CH *p*-tolylN), 6.96 (d, J_{HH} = 7.8 Hz, 2H CH *p*-tolylN), 6.8 (s, 1H *p*-CH Ar), 6.75 (s, 2H *o*-CH Ar) 5.17 (s, 2H CH Cp), 4.35 (s, 2H CH Cp), 2.76 (s, 2H CH_2-CMe_2), 2.24 (s, 6H Me-Ar), 2.16 (s, 3H Me *p*-tolylN), 1.32 (s, 6H CMe_2), 1.01 (s, 18H PMe_3), 0.78 (s, free PMe_3). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: 255.30. ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25 ºC): δ 52.47 (plateau, $\Delta\nu_{top}$ = 2564), -60.5 (broad s, free PMe_3).

Generation of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)V(N-*p*-tolyl)(dmpe) (5.13)



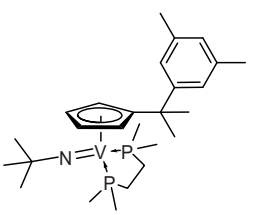
Dmpe (0.01 g, 0.05 mmol) was added into an NMR tube via a syringe to a solution of **5.6** (0.03 g, 0.05 mmol) in C_6D_6 (0.5 mL). Before heating the mixture at 50 °C, the tube was degassed at the vacuum line. After 4 days at 50 °C the methane was measured by Toepler pump (0.97 CH_4/V). The complex **5.13** had been generated in 95% yield. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 7.08 (d, J_{HH} = 8.2 Hz, 2H CH *p*-tolylN), 6.93 (s, 2H *o*-CH Ar), 6.89 (d, J_{HH} = 8.1 Hz, 2H CH *p*-tolylN), 6.81 (s, 1H *p*-CH Ar), 5.16 (td, J_{HH} = 4.5, 2.2 Hz, 2H CH Cp), 4.24 (td, J_{HH} = 5.7, 2.9 Hz, 2H CH Cp), 2.98 (s, 2H CH_2-CMe_2), 2.26 (s, 6H Me-Ar), 2.12 (s, 3H Me *p*-tolylN), 1.58 (m, 2H PCH_2), 1.37 (m, 6H PMe_2), 1.27 (m, 2H PCH_2), 1.17 (s, 6H CMe_2), 0.80 (m, 6H PMe_2). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6 , 25°C): δ 139.50 (*ipso*-C Ar), 136.24 (*ipso*-C *p*-tolylN), 129.18 (CH *p*-tolylN), 128.69 (CH Ar), 128.51 (*ipso*-C *p*-tolylN), 127.42 (CH *p*-tolylN), 125.44 (CH Ar), 93.74 (CH Cp), 86.84 (CH Cp), 51.87 (CH CH_2-bridge), 36.05 (C-bridge Ar-Cp), 31.66 (PCH_2), 28.80 (CH_3 Ar), 23.56 (PMe_2), 21.22 (CMe_2), 20.83 (PMe_2), 20.77 (Me *p*-tolylN). ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25°C): δ 88.86 (plateau, $\Delta\nu_{top}$ = 2303). ^{51}V NMR (131.4 MHz, C_6D_6, 25ºC) δ: -27.96.

Generation of (η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(PMe_3)$_2$ (5.14)



A solution of **5.8** (0.02 g, 0.05 mmol) in 0.6 mL C_6D_6 was placed in an NMR tube and PMe_3 was added (0.01 g, 0.01 mL, 0.10 mmol) via syringe at room temperature. The tube was attached to a vacuum line and degassed three times, after which it was placed at 50 °C and kept at this temperature for 6 days. After this time the amount of methane was measured by Toepler pump [0.90 CH_4/V]. The volatiles were transferred *in vacuo* and analyzed by ^{1}H NMR spectroscopy and GC-Ms. The spectroscopic analysis confirmed the presence of *N*-isopropyl-2-propanimine. The presence of Cp_2Fe as internal standard, methane measured and the imine released confirmed the formation of compound **5.14** in 90% yield. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 6.91 (s, 2H *o*-CH Ar), 6.83 (s, 1H *p*-CH Ar), 4.74 (s, 2H CH Cp), 4.34 (s, 2H CH Cp), 2.92 (s, 2H CH_2-CMe_2), 2.29 (s, 6H CH_3 Ar)), 1.46 (s, 9H CH_3 *t*-Bu), 1.07 (m, 18H PMe_3). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6, 25 °C): δ 161.84 (*ipso*-C Ar), 153.97 (*ipso*-C Ar), 137.56 (CH Ar), 127.93 (CH Ar), 93.61 (br, CH Cp), 90.83 (CH Cp), 51.44 (CH *C*H_2-bridge), 39.27 (C-bridge Ar-Cp), 29.84 (*ipso*-C *t*-Bu), 25.94 (CH_3 Ar), 25.88 (CH_3 P*Me*$_3$) , 25.84 (CH_3 P*Me*$_3$), 25.80 (CMe_2), 24.6 (CH_3 *t*-Bu), 22.478 (CMe_2). ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 54.38 ppm ($\Delta\nu_{top}$= 2496). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -61.78 (t, $J_{V\text{-}P}$ = 369.70 Hz).

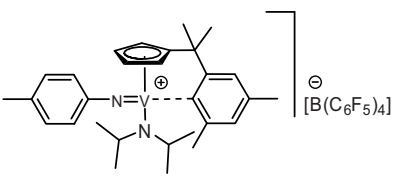
Generation of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(dmpe) (5.15)



To a benzene-d_6 (0.5 mL) solution of **5.7** (0.02 g, 0.05 mmol), dmpe (0.01 g, 0.01 mL, 0.05 mmol) was added via syringe and the mixture was put it into an NMR tube. The tube was attached to vacuum line and degassed three times. While keeping the tube at 50 °C for 6 days the compound **5.15** was generated in 88 % yield. The amount of methane was measured by Toepler pump [0.94 CH_4/V]. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 7.50 (s, 2H *o*-CH Ar), 6.78 (s, 1H *p*-CH Ar), 5.02 (broad, 2H CH Cp), 4.37 (broad, 2H CH Cp), 2.25 (s, 6H Me-Ar), 1.69 (s broad, 6H PMe_2), 1.38 (broad, 9H *t*-BuN overlap with 3H CMe_2), 1.29 (m, 2H P*C*H_2), 1.10 (broad 2H P*C*H_2), 0.80 (s, 3H CMe_2), 0.60 (broad, 6H PMe_2). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6 , 25 °C): δ 152.98 (*ipso*-C Ar), 137.05 (*ipso*-C Ar), 127.32 (CH Ar), 125.0 (CH Ar), 124.18 (*ipso*-C Cp), 94.05 (broad CH Cp), 84.94 (CH Cp), 32.38 (P*C*H_2), 28.09 (CH_3 Ar),

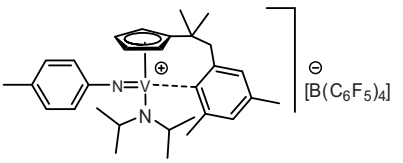
21.80 (CH_3 *t*-Bu), 18.63 (P*Me*$_2$), 13.92 (P*Me*$_2$), 13.83 (CMe_2), 13.80 (CMe_2), 13.74. ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ 89.50 (plateau, $\Delta\nu_{top}$ = 2252). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -342.88.

Synthesis of [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)][$B(C_6F_5)_4$] (5.16)



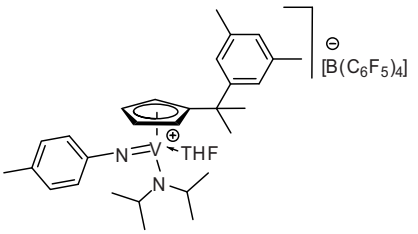
To a solution of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)VMe(*p*-tolylN) (**5.5**) (0.07 g, 0.15 mmol) in 1 mL of dichloromethane was added [Ph_3C][$B(C_6F_5)_4$] (0.14 g, 0.15 mmol) in 1 mL of dichloromethane. The reaction mixture was stirred for 1.5 h at room temperature after which the solvent was removed *in vacuo*. Product **5.16** could be isolated as red oil. Crystallization from 1 mL dichloromethane layered with cyclohexane (2.5 mL) gave suitable crystals for X-ray analysis and an isolated yield of 0.16 g (0.14 mmol, 95 %). ^{1}H NMR (500 MHz, CD_2Cl_2, -10 °C): δ 7.29 (d, J_{HH} = 8.3 Hz, 2H CH *p*-tolylN), 7.21 (d, J_{HH} = 8.3 Hz, 2H, *p*-tolylN), 7.07 (s, 1H, Ar *p*-H), 6.99 (s, 1H, Ar *o*-H), 6.04 (dd, *J* = 5.1, 3.1 Hz, 1H Cp), 6.00-5.96 (m, 2H Cp), 5.73 (dd, *J* = 5.2, 2.2 Hz, 1H Cp), 5.25 (s, 1H, Ar *o*-H), 3.67 (sept., J_{HH} = 6.6 Hz, 1H CH *i*-Pr), 3.61 (sept., J_{HH} = 6.5 Hz, 1H CH *i*-Pr), 2.53 (s, 3H, CH_3 *p*-tolyl), 2.47 (s, 3H, CH_3-Ar), 2.45 (s, 3H, CH_3-Ar), 1.95 (s, 3 H, CMe_2), 1.89 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.55 (s, 3 H, CMe_2), 1.26 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 0.95 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 0.52 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H} NMR (125.7 MHz, CD_2Cl_2, -10 °C): δ 157.45 (*ipso*-C Ar), 156.47 (*ipso*-C Ar), 148.41 (*ipso*-C *p*-tolylN), 148.18 (d, J_{CF} = 240.1 Hz, *o*-CF B(C_6F_5)$_4$), 139.93 (*ipso*-C *p*-TolylN), 138.30 (d, J_{CF} = 240.0 Hz, *p*-CF B(C_6F_5)$_4$), 136.38 (d, J_{CF} = 244.7 Hz, *m*-CF B(C_6F_5)$_4$), 131.21 (CH *p*-tolylN), 129.86 (CH *p*-tolylN), 125.71 (CH Ar), 123.44 (br, *ipso*-C B(C_6F_5)$_4$), 118.97 (CH Ar) 109.81 (CH, Cp), 109.19 (CH, Cp), 106.46 (CH, Cp), 100.14 (CH, Cp), 93.77 (CH Ar), 67.69 (CH *i*-Pr), 60.26 (CH *i*-Pr), 37.99 (C-bridge Ar-Cp), 33.01 (CH_3 *i*-Pr), 27.32 (CH_3 Ar), 26.37 (CH_3 *i*-Pr), 24.57 (CH_3 *p*-tolylN), 23.34 (CMe_2), 22.96 (CMe_2), 21.36 (CH_3), 20.62 (CH_3 *i*-Pr), 18.66 (CH_3 i-Pr). ^{19}F {^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ -132.18 (*o*-F), -162.51 (*p*-F), -166.35 (*m*-F). ^{51}V NMR (131.4 MHz, CD_2Cl_2, -10 ºC) δ: -408.41. Anal. Calcd.(%) for $C_{53}H_{40}N_2VBF_{20}$: C, 55.52; H, 3.52; N, 2.44. Found: C, 54.10; H, 3.69; N, 2.25.

Generation of [(η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)] [$B(C_6F_5)_4$] (5.17)



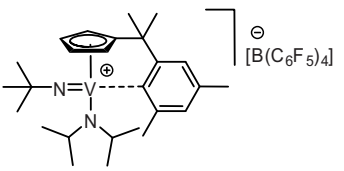
A cold (-10 °C) solution of [Ph_3C][$B(C_6F_5)_4$] (0.05 g, 0.05 mmol) in 0.5 mL of dichloromethane-d_2 was added to **5.6** (0.03 g, 0.05 mmol). The color immediately changed from yellowish brown to intense red. The cationic species **5.17** was generated *in situ* quantitatively. ^{1}H NMR (500 MHz, CD_2Cl_2, -10 °C): δ 7.41 (d, J_{HH} = 8.3 Hz 2H *p*-tolylN), 7.33-7.25 (m, 6H CH Ph_3CMe), 7.23-7.18 (m, 6H CH Ph_3CMe), 7.09 (d, J_{HH} = 7.3 Hz, 3H CH Ph_3CMe overlap with 2H *p*-tolylN), 7.04 (s, 1H CH Ar), 6.95 (s, 1H CH *o*-Ar), 6.47 (dd, J_{HH} = 3.3, 2.2 Hz, 1H Cp), 6.10 (dd, J_{HH} = 2.8, 2.2 Hz, 1H Cp), 6.08 (dd, J_{HH} = 3.1 2.0 Hz, 1H Cp), 5.57 (s, 1H CH *o*-Ar), 5.20 (dd, J_{HH} = 3.0, 2.4 Hz, 1H Cp), 4.47 (sept, J_{HH} = 6.3 Hz, 1H CH *i*-Pr), 3.68 (sept, J_{HH} = 6.3 Hz, 1H CH *i*-Pr), 3.17 (d, J_{HH} = 14.1 Hz, 1H CH_2-bridge), 2.85 (d, J_{HH} = 14.0 Hz, 1H CH_2-bridge), 2.46 (s, 3H CH_3 *p*-tolyl), 2.32 (s, 6H CH_3-Ar), 2.17 (s, 3H CH_3, Ph_3CMe), 1.85 (d, J_{HH}=6.3 Hz, 3H CH_3 *i*-Pr), 1.64 (s, 3H CMe_2), 1.51 (s, 3H CMe_2), 1.21 (d, J_{HH} = 6.4 Hz, 3H CH_3 *i*-Pr), 1.11 (d, J_{HH} = 6.2 Hz, 3H CH_3 i-Pr), 0.62 (d, J_{HH} = 6.2 Hz, 3H CH_3 i-Pr). ^{13}C {^{1}H} NMR (125.7 MHz, CD_2Cl_2, -10 °C): δ 159.35 (*ipso*-C Ar), 157.32 (*ipso*-C Ar), 149.79 (*ipso*-C *p*-tolylN), 149.12 (CH *p*-tolylN), 148.04 (d, J_{CF} = 241.2 Hz, *o*-CF B(C_6F_5)$_4$), 145.47 (*ipso*-C *p*-tolylN), 140.16 (*ipso*-C Ph_3CMe), 138.21 (d, J_{CF} = 240.5 Hz, *p*-CF B(C_6F_5)$_4$), 136.25 (d, J = 241.0 Hz, *m*-CF B(C_6F_5)$_4$), 131.17 (CH Ar), 130.58 (*ipso*-C Cp), 129.85 (CH *p*-tolylN), 128.72 (CH Ph_3CMe), 127.95 (CH Ph_3CMe), 126.35 (CH Ar), 126.05 (CH Ph_3CMe), 123.75 (br, *ipso*-C B(C_6F_5)$_4$), 112.95 (CH Cp), 109.09 (CH Cp), 101.48 (CH Ar), 100.35 (CH Cp), 98.16 (CH Cp), 68.40 (CH *i*-Pr), 60.10 (CH *i*-Pr), 52.44 (CH CH_2-bridge), 49.62 (C_q-bridge Ar-Cp), 40.15 (C_q, Ph_3CMe), 32.94 (CH_3, *i*-Pr), 32.25 (CH_3, *i*-Pr), 30.25 (CH_3 Ph_3CMe), 26.90 (CH_3, *i*-Pr), 26.04 (CH_3 Ar), 23.77 (CMe_2), 22.27 (CMe_2), 21.39(CH_3 *p*-tolylN), 21.26 (CH_3, *i*-Pr). ^{19}F {^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ -133.42 (broad s, *o*-F B(C_6F_5)$_4$), -163.97 (t, J = 20.4 Hz, *p*-F B(C_6F_5)$_4$), -167.83 (t, J = 17.3 Hz, m-F, B(C_6F_5)$_4$). ^{51}V NMR (131.4 MHz, CD_2Cl_2, -10 ºC) δ: -253.53.

[(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*p*-tolyl)(THF)][$B(C_6F_5)_4$] (5.18)



To a freshly generated cationic species **5.16** in dichloromethane, a few drops of THF-d_8 were added forming immediately the vanadium-THF adduct species **5.18**. ^{1}H NMR (500 MHz, CD_2Cl_2, -10 °C): δ 7.25 (d, J_{HH} = 7.54 Hz, 2H CH *p*-tolylN), 7.08 (d, J_{HH} = 8.12 Hz, 2H CH *p*-tolylN), 6.79 (s, 1H CH Ar *p*-H), 6.76 (s, 2H, Ar *o*-H), 6.57 (s, 1H CH Cp), 6.49 (s, 1H CH Cp), 6.12 (s, 1H CH Cp), 6.04 (s, 1H CH Cp), 5.50 (sept., J_{HH} = 6.3 Hz, 1H CH *i*-Pr), 3.90 (sept., J_{HH} = 6.2 Hz, 1H CH *i*-Pr), 2.42 (s, 3H, CH_3 *p*-tolyl), 2.20 (s, 6H CH_3-Ar), 1.74 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr), 1.48 (d, J_{HH} = 6.1 Hz, 3H CH_3 *i*-Pr), 1.34 (s, 6H CMe_2), 1.26 (d, J_{HH} = 5.9 Hz, 3H CH_3 *i*-Pr), 1.11 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr). ^{51}V NMR (131.4 MHz, CD_2Cl_2, -10 ºC) δ: -383.05.

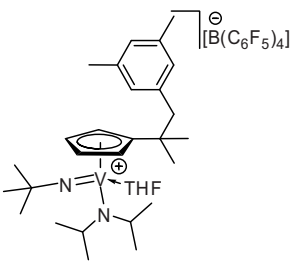
Generation of [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)][$B(C_6F_5)_4$] (5.19)



$[Ph_3C][B(C_6F_5)_4]$ (0.04 g, 0.05 mmol) was added to a solution of **5.7** (0.02 g, 0.05 mmol) in C_6D_5Br (0.5 mL) in an NMR tube at room temperature. The color of the solution changed immediately from brown-green to red, indicating stoichiometric generation of the cationic species **5.19**. ^{1}H NMR (500 MHz, C_6D_5Br, -20 °C): δ 7.18-7.02 (m, 15H Ph_3CMe overlap with solvent), 6.62 (s, 1H Ar *o*-H), 6.45 (s, 1H Ar *p*-H), 5.68 (s, 1H Cp), 5.57 (s, 1H Cp), 5.55 (s, 1H Cp), 5.10 (s, 1H Cp), 4.64 (broad s, 1H Ar *o*-H), 3.10 (sept, J_{HH} = 6.2 Hz, 1H CH *i*-Pr), 2.99 (sept, J_{HH} = 6.0 Hz, 1H CH *i*-Pr), 2.23 (s, 3H CH_3-Ar), 2.10 (s, 3H CH_3-Ar), 2.04 (s, 3H CH_3 Ph_3CMe), 1.52 (d , J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr overlap with 3H of CMe_2), 1.24 (s, 9H CH_3 *t*-BuN), 1.10 (s, 3H CH_3 CMe_2), 0.79 (d, J_{HH} = 6.1 Hz, 3H CH_3 *i*-Pr), 0.56 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr), 0.18 (d, J_{HH} = 6.2 Hz, 3H CH_3 *i*-Pr). ^{13}C {^{1}H}NMR (125.7 MHz, C_6D_5Br, -20 °C): δ 156.22 (*ipso*-C Ar), 154.83 (*ipso*-C Ar), 150.92, 148.85 (*ipso*-C Ph_3CMe), 148.36 (d, J_{CF} = 240.8 Hz, *o*-CF B(C_6F_5)$_4$), 138.26 (d, J_{CF} = 235.9 Hz, *p*-CF B(C_6F_5)$_4$), 136.34 (d, J_{CF} = 241.9 Hz, *m*-CF B(C_6F_5)$_4$), 128.65 (CH Ph_3CMe), 127.86 (CH Ph_3CMe), 127.29 (CH Ph_3CMe), 124.20 (br, *ipso*-C B(C_6F_5)$_4$), 118.02 (CH Ar), 110.01(CH Ar), 105.46 (CH Cp), 103.42 (CH Cp), 97.24 (CH Cp), 91.02 (CH Cp), 79.15 (CH Ar), 67.08 (CH *i*-Pr) 58.65 (C_q-

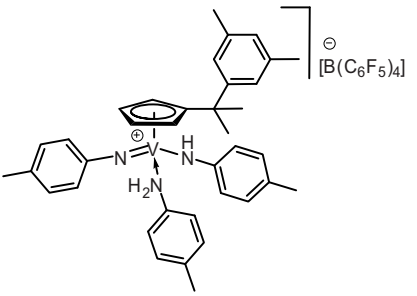
bridge Ar-Cp), 52.19 (CH *i*-Pr), 37.15 (C_q, Ph_3CMe), 32.79 (CH_3, *i*-Pr), 31.65 (CH_3 *t*-BuN), 30.22 (CH_3, Ph_3CMe), 26.06 (CH_3 Ar), 25.95 (CH_3 Ar), 24.37 (CMe_2), 23.27(CMe_2), 22.29 (CH_3, *i*-Pr), 19.61 (CH_3, *i*-Pr), 18.82 (CH_3, *i*-Pr), C_q of *t*-BuN not observed. ^{19}F {^1H} NMR (100 MHz, C_6D_5Br, 25 °C): δ -132.15 (broad s, *o*-F $B(C_6F_5)_4$), -162.57 (t, J = 20.9 Hz, *p*-F $B(C_6F_5)_4$), -166.40 (t, J = 17.1 Hz, m-F, $B(C_6F_5)_4$). The same cationic species was also generated in CD_2Cl_2. ^{51}V NMR (131.4 MHz, CD_2Cl_2, 25ºC) δ: -475.38.

Generation of [(η^5-$C_5H_4CMe_2CH_2$-3,5-$Me_2C_6H_3$)(*i*-Pr_2N)V(N-*t*-Bu)(THF)] [$B(C_6F_5)_4$] (5.20)



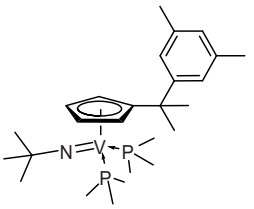
To a solution of **5.8** (0.02 g, 0.04 mmol) in 0.5 mL THF-d_8, $[Ph_3C][B(C_6F_5)_4]$ (0.04 g, 0.04 mmol) was added at room temperature. The cationic vanadium-THF adduct species **5.20** was quantitatively generated. ^1H NMR (500 MHz, THF-d_8, 20 °C): δ 7.29-7.03 (m, 15H Ph_3CMe), 6.81 (s, 1H CH Ar), 6.52 (td, J_{HH} = 3.0, 2.1 Hz, 1H Cp), 6.44 (td, J_{HH} = 3.0, 2.1 Hz, 1H Cp), 6.39 (s, 2H CH Ar), 6.18 (dt, J_{HH} = 3.1, 2.2 Hz, 1H Cp), 6.07 (dd, J_{HH} = 5.2, 2.9 Hz, 1H Cp), 5.59 (sept., J_{HH} = 6.3 Hz, 1H CH *i*-Pr), 3.98 (sept., J_{HH} = 6.4 Hz, 1H CH *i*-Pr), 2.69 (d, J_{HH} = 12.68 Hz, 1H CH_2-bridge), 2.66 (d, J_{HH} = 12.61 Hz, 1H CH_2-bridge), 2.18 (s, 6H CH_3-Ar), 2.15 (s, 3H CH_3 Ph_3CMe), 1.83 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 1.56 (s, 9H CH_3 *t*-BuN), 1.55 (s, 3H CH_3 CMe_2), 1.49 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr), 1.29 (d, J_{HH} = 6.3 Hz, 3H CH_3 *i*-Pr), 1.20 (d, J_{HH} = 6.5 Hz, 3H CH_3 *i*-Pr). ^{13}C {^1H}NMR (125.7 MHz, THF-d_8, 20 °C): δ 151.12 (*ipso*-C Ar), 150.16 (d, J_{CF} = 240.5 Hz, *o*-CF $B(C_6F_5)_4$) 140.17 (*ipso*-C Ar), 140.12 (d, J_{CF} = 240.9 Hz, *p*-CF $B(C_6F_5)_4$), 139.00, 138.58, 138.11 (d, J_{CF} = 245.6 Hz, *m*-CF $B(C_6F_5)_4$), 130.54, 130.13, 129.53, 127.64, 112.71 (CH Cp), 109.58 (CH Cp), 109.25 (CH Cp), 106.35 (CH Cp), 71.85(CH *i*-Pr) , 61.34 (CH *i*-Pr), 54.82 (CH CH_2-bridge), 52.40 (C, Ph_3CMe), 39.46 (C_q-bridge Ar-Cp), 33.94 (CH_3, *i*-Pr), 33.49 (CH_3 *t*-BuN), 31.85 (CH_3, Ph_3CMe), 29.77 (CH_3, *i*-Pr), 28.81 (CH_3 Ar), 28.22 (CH_3, *i*-Pr), 24.20 (CMe_2), 23.34 (CMe_2), 22.30 (CH_3, *i*-Pr). ^{19}F {^1H} NMR (100 MHz, CD_2Cl_2, 20 °C): δ -133.18 (broad s, *o*-F $B(C_6F_5)_4$), -165.41 (t, J = 20.3 Hz, *p*-F $B(C_6F_5)_4$), -167.83 (t, J = 17.2 Hz, m-F, $B(C_6F_5)_4$). ^{51}V NMR (131.4 MHz, THF-d_8, 20 ºC) δ: -446.64.

Generation of [(η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)(*p*-tolylNH)V(N-*p*-tolyl)(H_2N-*p*-tolyl][$B(C_6F_5)_4$] (5.21)



To a **5.16** (0.04 mmol) freshly generated solution in C_6D_5Br an excess of *p*-toluidine (0.04 g, 0.36 mmol) was added. After 1 h at room temperature the compound **5.21** had been generated stoichiometrically *in situ*. ^{1}H NMR (500 MHz, C_6D_5Br, 25 °C): δ 12.55 (s, 1H NH *p*-tolylN), 7.17-7.05 (m, 15H Ph_3CMe), 6.90 (d, J_{HH} = 8.0 Hz, 4H *p*-tolylN), 6.86 (d, J_{HH} = 7.96 Hz, 2H *p*-toluidine overlap with 4H *p*-tolylNH), 6.76 (s, 2H CH Ar), 6.72 (s, 1H CH Ar), 6.41 (d, J_{HH} = 8.0 Hz, 2H *p*-toluidine), 5.95 (t, J_{app} = 2.43 Hz, 2H Cp), 5.54 (t, J_{app} = 2.15 Hz, 2H Cp), 3.52 (broad s, NH *p*-toluidine), 2.76 (sept., J_{HH} = 6.3 Hz, 2H CH *i*-Pr), 2.17 (s broad, 3H CH_3 *p*-tolylN), 2.15 (s, 3H CH_3 *p*-tolylN), 2.14 (s, 3H CH_3 *p*-toluidine overlap with 3H CH_3 CMe_2), 2.04 (s, 3H CH_3, Ph_3C*Me*), 1.27 (s, 3H CH_3 CMe_2), 0.88 (d, J_{HH} = 6.3 Hz, 12H CH_3 i-Pr). ^{13}C {^{1}H} NMR (125.7 MHz, C_6D_5Br, 25°C): δ 148.97 (*ipso*-C, *p*-toluidine), 148.54 (d, J_{CF} = 243.7 Hz, *o*-CF B(C_6F_5)$_4$), 146.62 (*ipso*-C *p*-Tolyl), 143.84 (*ipso*-C, *p*-toluidine), 140.08 (*ipso*-C *Ph*$_3$CMe), 138.39 (d, J_{CF} = 238.5 Hz, *p*-CF B(C_6F_5)$_4$), 137.75 (*ipso*-C *p*-tolyl), 136.47 (d, J_{CF} = 240.1 Hz, *m*-CF B(C_6F_5)$_4$), 131.22 (CH *p*-tolylN), 129.71 (CH *p*-toluidine), 128.66 (CH *Ph*$_3$CMe), 128.53 (CH *p*-tolylN), 127.79 (CH *Ph*$_3$CMe), 127.15 (CH *p*-tolylN), 125.86 (CH *Ph*$_3$CMe), 124.95 (br, *ipso*-C B(C_6F_5)$_4$), 123.88 (CH *p*-tolylN), 119.30, 115.17 (CH *p*-toluidine), 110.21 (CH Cp), 109.81 (CH Cp), 52.44 (C_q Ph_3*C*Me), 45.44 (CH *i*-Pr), 39.85 (C_q-bridge Ar-Cp), 30.38 (*C*H$_3$ Ph_3C*Me*), 30.36 (CH_3 Ar), 22.75(*C*H$_3$, *i*-Pr overlap with CMe_2), 21.32 (CMe_2), 20.56 (broad *C*H$_3$, *p*-tolyl), 20.38 (*C*H$_3$, *p*-toluidine). ^{19}F {^{1}H} NMR (100 MHz, C_6D_5Br, 25 °C): δ -132.22 (s, *o*-F B(C_6F_5)$_4$), -162.34 (t, *J* = 21.1 Hz, *p*-F B(C_6F_5)$_4$), -166.27 (t, *J* = 17.6 Hz, m-F, B(C_6F_5)$_4$).

Generation of (η^5-$C_5H_4CMe_2$-3,5-$Me_2C_6H_3$)V(N-*t*-Bu)(PMe_3)$_2$ (5.22)



PMe_3 was added (0.006 g, 0.008 mL, 0.08 mmol) to a solution of **5.7** (0.02 g, 0.04 mmol) in C_6D_6 (0.5 mL). The NMR tube was placed at 50 °C over 5 days, after which the ^{1}H NMR spectroscopy showed quantitative formation of complex **5.22** together with methane liberation and *N*-isopropyl-2-propanimine. ^{1}H NMR (500 MHz, C_6D_6, 25°C): δ 7.40 (s, 2H *o*-CH Ar), 6.77 (s, 1H *p*-CH Ar), 4.99 (br, 2H CH Cp, $\Delta\nu_{1/2}$ = 78 Hz), 4.41 (br, 2H CH Cp, $\Delta\nu_{1/2}$ = 60 Hz), 2.25 (broad, 6H Me-Ar), 1.55 (s, 6H CMe_2), 1.49 (s, 9H *t*-BuN), 1.06 (s, 18H PMe_3), 0.79 (s, free PMe_3). ^{13}C {^{1}H}NMR (100 MHz, C_6D_6, 25 °C): δ 161.425 (*ipso*-C Ar), 153.124 (*ipso*-C Ar), 136.917 (CH Ar), 127.166 (CH Ar), 124.712, 92.64 (CH Cp), 90.42 (CH Cp), 29.12 (CH_3 Ar), 23.97 (CH_3 P*Me*$_3$), 23.61 (CMe_2), 21.68 (CH_3 *t*-Bu). ^{51}V NMR (131.4 MHz, C_6D_6, 25 ºC) δ: -64.23. ^{31}P {^{1}H} NMR (100 MHz, C_6D_6, 25°C): δ 54.70 (plateau, $\Delta\nu_{top}$ = 2454.2), -61.24 (broad s, free PMe_3).

Catalytic cyclotrimerization of phenylacetylene with *ansa*-Cp-arene vanadium cationic 5.16, 5.19 and 5.20. The cyclotrimerization experiments of the phenylacetylene were performed on NMR-scale using an NMR tube with a Teflon (Young) valve. The experimental procedure was followed as previously described in Chapter 3 and 4.

Catalytic hydroamination of PhCCH with *p*-toluidine using cationic vanadium complex 5.21. All hydroamination experiments were performed on NMR scale in NMR tubes with a Teflon (Young) valve. To a freshly prepared solution of **5.16** (0.029 g, 0.025 mmol) in 0.6 mL C_6D_5Br, 10 equivalents of *p*-toluidine (0.027 g, 0.25 mmol) was added generating in situ, after 1 h at ambient temperature, the vanadium complex **5.21**. Subsequently, 10 equivalents of alkyne (*i.e* PhCCH 0.026 g, 0.25 mmol) was added to the reaction mixture. The tube was placed at 80 ºC and monitored by ^{1}H NMR spectroscopy until full conversion (in general) of the alkyne. Apart from the ^{1}H NMR spectroscopy, the reaction mixtures were analyzed by GC-MS and GC as well. The same procedure was applied also when different ratios of PhCCH : *p*-toluidine were employed (*e.g.*, 2:1 and 3:1 ratio).

X-ray crystal structures. Suitable crystals of **5.1**, **5.4**, **5.5** and **5.16** were mounted on top of a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream on a Bruker22 SMART APEX CCD diffractometer. The final unit cell was obtained from the xyz centroids of 5173 (**5.1**), 1626 (**5.4**), 3279 (**5.5**) and 5280 (**5.16**) reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*).[29] The structures were solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF[30] A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined. All refinement and geomatry calculations were performed with the program packages *SHELXL*[31] and *PLATON*.[32] Crystal data and details on data collection and refinement are presented in Table 7 and 8.

Table 7. Crystallographic data for **5.1** and **5.4**

	5.1	***5.4***
chem formula	$C_{29}H_{40}ClN_2V$	$C_{27}H_{44}ClN_2V$
Fw	503.04	483.05
crystal system	monoclinic	triclinic
color, habit	red, platelet	red, platelet
size, mm	0.49 x 0.15 x 0.08	0.46 x 0.39 x 0.20
space group	$P2_1/n$	P-1
a, Å	10.830(2)	13.254(7)
b, Å	12.469(2)	14.630(8)
c, Å	20.507(4)	15.021(8)
α, (°)	-	86.012(6)
β, (°)	101.873(3)	89.735(7)
γ, (°)	-	70.819(6)
V, Å^3	2710.0(8)	2744(3)
Z	4	4
ρ_{calc}, g.cm^{-3}	1.196	1.169
F(000)	1012	1040
μ(Mo K$\overline{\alpha}$), cm^{-1}	4.82	4.75
temperature (K)	100(1)	100(1)
θ range (°)	2.52 - 26.69	2.53, 25.03
min and max transm	0.7235 – 0.9624	0.7939 – 0.9095
R(F)	0.0591	0.0823
wR(F^2)	0.1605	0.2446
GooF	1.040	1.022
observed reflns $F_o \geq 4.0\ \sigma\ (F_o)$)	3060	4150
data collected (h, k, l)	-12:12; -14:14; -24:23	-15:14; -17:17; -17:15
params refined	351	581

Table 8. Crystallographic data for **5.5** and **5.16**.

	5.5	***5.16***
chem formula	$C_{30}H_{43}N_2V$	$[C_{29}H_{40}N_2V]^+$ $[C_{24}BF_{20}]^-$
Fw	482.63	1146.62
crystal system	triclinic	monoclinic
color, habit	red, block	red, platelet
size, mm	0.37 x 0.29 x 0.22	0.47 x 0.28 x 0.19
space group	*P*-1	$P2_1/n$
a, Å	9.1038(7)	15.858(2)
b, Å	11.4794(8)	15.996(2)
c, Å	13.9541(10)	20.876(2)
α, (°)	102.4383(12)	-
β, (°)	99.1711(12)	104.360(2)
γ, (°)	101.4992(12)	-
V, Å^3	1363.93(17)	5130.1(10)
Z	2	4
ρ_{calc}, g.cm^{-3}	1.175	1.485
F(000)	520	2320
μ(Mo K$\overline{\alpha}$), cm^{-1}	3.83	3.05
temperature (K)	100(1)	100(1)
θ range (°)	2.51 - 27.98	2.25 - 28.30
min and max transm	0.8579 – 0.9205	0.8465 – 0.9437
R(F)	0.0438	0.0432
wR(F^2)	0.1148	0.1106
GooF	1.004	1.022
observed reflns $F_o \geq 4.0\ \sigma\ (F_o)$)	4103	8324
data collected (h, k, l)	-11:11; -13:14; -17:17	-20:20; -20:20; -25:26
params refined	308	854

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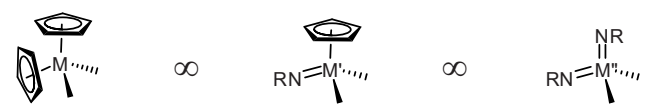
Samenvatting

Vanadium is een uitdagend metaal om mee te werken. Dit blijkt al bij de ontdekking of eigenlijk, dubbele ontdekking van vanadium. In 1801 ontdekte Andres Manuel del Rio uit Mexico een nieuw element en noemde het 'panchromium' omdat het metaal eigenschappen vertoonde overeenkomstig met chroom. Later veranderde de naam in erythronium omdat de meeste zouten van dit metaal rood kleurden als ze verhit werden. (erythrocyte is Grieks voor rode bloedcel). De naam vanadium werd dertig jaar later aan het metaal gegeven toen het in 1831 werd herontdekt door de zweed Gabriel Sefström. Vanadium stamt af Vanadis, de Godin van schoonheid en vruchtbaarheid voor Noord Germaanse stammen. Sefström koos voor deze naam omdat stoffen met vanadium als bestandsdeel een verscheidenheid aan prachtige kleuren vertonen.

Vanadium is uit chemisch oogpunt een van de meest boeiende metalen van de vroege overgangsmetalen. Dit vanwege het feit dat vanadium een grote verscheidenheid oxidatie niveaus (-1 t/m +5) kan aannemen en daardoor een breed spectrum aan reactiviteit vertoont. Het is dan ook niet vreemd dat vanadiumstoffen, in het bijzonder de katalytische eigenschappen, intensief onderzocht zijn. Zo is de ontdekking van Ziegler-Natta polymerisatie van α-olefinen een van de belangrijkste drijfveren geweest achter het onderzoek om vanadium toe te passen als katalysator voor dit type polymerisatie. Tijdens de jaren tachtig en negentig is dan ook veel vooruitgang geboekt in het design en de activiteit van katalysatoren voor α-olefinen polymerisatie met gebruik van vroege overgangsmetalen. De meest gebruikte katalysatoren zijn metallocenen met een metaal uit groep vier.

Het ontwikkelen van nieuwe non-metallocene katalysatoren gebaseerd op de isolobal analogie heeft ondermeer geleid tot onderzoek naar de toepassing van het imido ligand. Met succes werden katalysatoren met groep 5 metalen vanadium, niobium, tantalum en groep 6 metalen ontwikkeld (Schema 1).



M = Ti, Zr, Hf M' = V, Nb, Ta M" = Cr, Mo, W

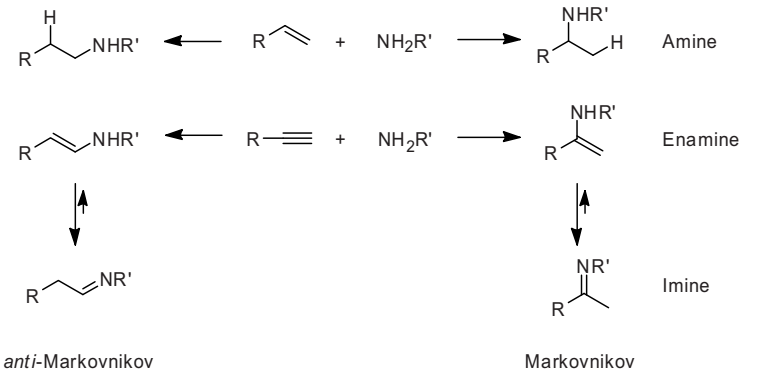
Schema 1

Één van de voorwaarden voor overgangsmetaal gekatalyseerde processen is dat het metaal deeltje elektronen arm is. Bijvoorbeeld, voor effectieve olefine polymerisatie is een metaaldeeltje nodig met 14 valentie elektronen of minder.

Kationische elektron arme katalysatoren zijn in het algemeen de meest effectieve katalysatoren voor dit type katalyse en grofweg 3 methoden zijn beschikbaar om kationische complexen te synthetiseren uit neutrale metaalalkyl katalysator precursoren. Ten eerste door alkyl abstractie met behulp van Lewis-zuren zoals $[Ph_3C][B(C_6F_5)_4]$ en $B(C_6F_5)_3$ wat het kationisch metaal complex genereert met als bijproduct het gemethyleerde Lewis-zuur. Ten tweede door protonering van het alkyl ligand met een Brønsted-zuur $[PhNHMe_2][BAr_4]$ (Ar = C_6H_5, C_6F_5) gevolgd door dissociatie, wat het kationisch metaal complex met als bijproduct het alkaan oplevert. Tot slot kan een kationisch metaal complex gegenereerd worden door halogeen abstractie van metaal-halogeen precursoren met zilver of thallium zouten.

Het imido ligand kan zoals gezegd het cyclopentadienyl ligand vervangen, op basis van de isolobal analogie, om nieuwe non-metalloceen katalysatoren te ontwikkelen. Tevens kan de stikstof-metaal dubbele binding, of in het geval van een stikstof-metaal enkelvoudige binding (amido), zelf reacties met andere functionele groepen ondergaan. Echter de chemie van dit soort omzettingen is in vergelijking met de chemie van koolstof-metaal bindingen nog relatief onbekend terrein.

Een van de meest bekende en onderzochte omzettingen waarin stikstof-metaal bindingen een rol spelen is de overgangmetaal gekatalyseerde hydroaminering. Bij deze omzetting wordt effectief een N-H groep geaddeerd aan een onverzadigde koolstof-koolstof binding en is de meest directe en efficiënte methode van amine alkylering (Schema 2).



Schema 2

De hydroaminering van onverzadigde koolstof-koolstof bindingen kan in principe 2 regio-isomeren als product opleveren; het zogenaamde Markovnikov en *anti*-Markovnikov product (Schema 2). Het onderzoek naar actieve en regioselectieve katalysatoren heeft katalysatoren met grote verscheidenheid aan gebruikte metalen opgeleverd. Complexen van de zeldzame aardmetalen (scandium, yttrium en 14 van de lantaniden) leveren actieve en selectieve katalysatoren op voor *intra*molecular hydroamineringen, echter *inter*moleculaire omzettingen zijn lastiger en tot nu toe zijn maar een beperkt aantal goede katalysatoren gebaseerd op een zeldzaam aardmetaal ontwikkeld. Op basis van late overgangsmetalen zijn katalysatoren ontwikkeld voor *intra*moleculaire hydroamineringen met een hoge functionele groep tolerantie. Palladium is het bekendste en meest gebruikte late overgangsmetaal voor de hydroaminering van alkynen. *Inter*moleculaire hydroaminering bleek ook voor dit type katalysatoren lastiger en slechts een aantal voorbeelden van dit type gekatalyseerde omzettingen zijn beschreven. Complexen van de vroege overgangsmetalen. met name titaanverbindingen, zijn uitgebreid onderzocht als katalysatoren voor *intra* en *inter*moleculaire hydroaminering. Actieve en selectieve katalysatoren voor zowel *intra*- als *inter*moleculaire hydroamineringen zijn beschreven met complexen van groep 4 metalen. Groep 5 metalen vertonen ook katalytische activiteit in de hydroaminering alleen de activiteit is in het algemeen lager dan voor complexen van groep 4 metalen.

Het wordt aangenomen dat voor *inter*moleculaire hydroamineringen gekatalyseerd door complexen van vroege overgangsmetalen het katalytisch actieve deeltje een

metaal-imido binding moet hebben, hoewel insertie van de onverzadigde koolstof-koolstof binding in de amido binding niet uitgesloten kan worden. Sterker nog, het is bekend dat de metaal-imido binding van het kationische cyclopentadienyl-amido complex $[(\eta^5\text{-}C_5H_4C_2H_4N\text{-}i\text{-}Pr)V(N\text{-}t\text{-}Bu)(BrC_6H_5)]$ $[MeB(C_6F_5)_3]$ niet met onverzadigde substraten reageert en dat acetylenen in de vanadium-stikstof (amido) binding inserteren. Het doel van dit proefschrift is dan ook het onderzoeken van de relatieve reactiviteit van de metaal-amido en metaal-imido bindingen van half sandwich vanadium (V) complexen in het algemeen en in het bijzonder de katalytische activiteit van deze verbindingen in de hydroaminerings reactie.

In **hoofdstuk 2** wordt de synthese en karakterisatie van een reeks neutrale en kationische vanadium(V) amido-imido complexen beschreven. Voor de synthese van deze elektron arme vanadium complexen uit neutrale vanadium methyl complexen werden verschillende alkyl abstractie reagentia gebruikt. Daarbij reageerden de neutrale half-sandwich (*p*-tolylimido) vanadium(V) amido methyl complexen en de eerder beschreven linked $(\eta^5\text{-}C_5H_4C_2H_4N\textit{i}\text{-}Pr)V(N\text{-}t\text{-}Bu)Me$ complexen verschillend met Brønsted-zuren zoals $[PhNMe_2H]^+$. Tijdens deze synthesen werd ook duidelijk dat de Lewis-zure complexen gestabiliseerd kunnen worden door de coördinatie van een Lewis-base aan het metaal deeltje.

De thermische stabiliteit van neutrale half-sandwich vanadium(V) amido-imido complexen wordt beschreven in **hoofdstuk 3**. De thermolyse van deze neutrale complexen genereert in een aantal gevallen het CpV(III)-imido complex. Het synthetiseren van dit soort deeltjes zonder gebruik van een externe reductor is nog niet eerder beschreven in de literatuur. Deze laag valente deeltjes kunnen worden ‘gevangen’ door bijvoorbeeld phosphine liganden en geïsoleerd. Met X-ray diffractie werd kristalstructuren van een aantal derivaten bepaald.

In **hoofdstuk 4** wordt het onderzoek naar de reactiviteit van verschillende vanadium(V) amido-imido complexen in de hydroaminering van eindstandige en interne alkynen met *p*-toluidine of *tert*-butylamine beschreven. De katalytische activiteit van de vanadium complexen bleek lager dan die van de isoelectronische neutrale titaan verbindingen. Tevens bleek dat wanneer aromatische aminen gebruikt werden, mengsels van het Markovnikov product en gesubstitueerde

chinolinen als bijproduct verkregen werden. Deze chinolinen worden gevormd uit het *anti*-Markovnikov product tijdens de reactie. Sterisch gehinderde aminen zoals *t*-$BuNH_2$ leverden uitsluitend het *anti*-Markovnikov product op tijdens de hydroaminering van eindstandige alkynen.

De synthese en karakterisatie van neutrale en kationische cyclopentadienyl vanadium (V) imido-amido complexen met een pendant areen groep (zgn. *ansa* complexen) aan het cyclopentadienyl ligand wordt beschreven in **hoofdstuk 5**. Met X-ray diffractie werd bewijs geleverd voor een *intra*moleculaire η^1-areen binding tussen de pendant areen groep en het kationische vanadium deeltje. Met behulp van NMR spectroscopie is gekeken naar het dynamische (hemilabiele) gedrag van de kationische *ansa*-Cp-areen vanadium complexen. Uit deze experimenten bleek dat sterkte van de binding afneemt naarmate de lengte van de brug tussen het Cp-ligand en de areen toeneemt.

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